

**Abstracts**

**EUCHEM 2002**

# **MOLTEN SALTS CONFERENCE**

**St John's College, Oxford, UK  
1-6 September 2002**

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*EUCHEM 2002*  
**MOLTEN SALTS CONFERENCE**  
St John's College, Oxford, UK  
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## PREFACE

This book contains abstracts of the 6 plenary, 15 keynote lectures, 25 contributed oral presentations and 64 posters presented at EUCHEM 2002 Molten Salts Conference, St John's College, Oxford, 1-6 September 2002.

The first section contains the abstracts of the Plenary PL1-PL6 and Keynote Lectures K1-K15, the second section contains abstracts of the contributed oral presentations and last part the posters, which will be displayed throughout the conference.

Posters have been number consecutively as follows:

P1 – P64

Two formal poster viewing sessions have been scheduled to take place on:

**MONDAY 2 SEPTEMBER - 20:00**

Odd-numbered posters

and

**WEDNESDAY 4 SEPTEMBER – 20:00**

Even-numbered posters

Prior to the formal poster session there will be a poster animation session where presenters will be able to make a brief presentation about their work.

In addition, it is hoped that informal discussions of the posters may take place at other times throughout the meeting.

An index of the presenting authors can be found at the end of the book.

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Chemistry and physics of high and low temperature molten salts.

Applications of above in energy storage and generation, materials synthesis and waste processing.

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**PLENARY**

**LECTURES**

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## NOVEL MOLTEN SALT TECHNOLOGIES FOR THE PREPARATION OF METALS AND MATERIALS

Derek Fray

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Molten salts have been thoroughly investigated for over one hundred years and most of the fundamental properties are now known and this has enabled existing molten salt processes to be optimised with respect to current and energy efficiencies. Recently, many new processes have suggested and some of these are proceeding beyond laboratory scale experiments. These include processes such as metallothermic reduction of compounds where electron transfer plays an important part in the reduction reactions, electro-deoxidation where oxygen and other species are removed electrochemically from metal compounds when the compounds are made the cathode in a bath of calcium chloride or the chloride of some other electropositive element. This technology is very interesting in that alloys and intermetallic compounds can simply be made by the reduction of mixtures of metal oxides and this offers the opportunity to produce alloys and compounds that cannot be made by conventional processing. The application of this process will be discussed in relation to the production of novel alloys.

Other interesting concepts include the combination of solid electrolytes and molten salts to reduce metal compounds. For example, sodium can be produced by the electrolysis of sodium carbonate or sodium hydroxide and to prevent the sodium reacting with the electrolyte a sodium beta" alumina membrane is incorporated into the cell. This approach is being applied to the addition of sodium to molten aluminium. Solid oxide oxygen ion conducting membranes have also been incorporated into cells for the electrowinning of magnesium from magnesium chloride-neodymium oxy-chloride melts. The oxygen ion conductor separates the oxygen evolution reaction from magnesium deposition and if hydrogen is passed over the external surface of the electrolyte, the fuel cell effect will reduce the overall cell potential.

Another interesting concept is the use of centrifugal fields to help separate the anodic and cathodic products produced during the electrolysis of molten salts. The application of this approach to the electrowinning of zinc and lithium will be outlined.

The prospects for these exciting developments will be discussed.

## CURRENT RESEARCH ACTIVITIES ON THE TITANIUM REDUCTION PROCESS IN JAPAN

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The extensive research work by Fray and co-workers<sup>1-3</sup> on the direct electrochemical reduction of titanium dioxide ( $\text{TiO}_2$ ) to titanium in molten calcium chloride ( $\text{CaCl}_2$ ) has inspired not only Japanese research activity but has also stimulated the Japanese government and the titanium industry.

For a long time, a large variety of research work on the titanium reduction process was conducted in Japan, mostly at universities. However, most of this research was fundamental in nature and quite far from practical application. In the early 90s, a calcium-halide flux deoxidation technique<sup>4</sup> was developed through which titanium containing less than 100 ppm oxygen was produced directly from titanium alloys containing large amounts of oxygen. Further development was achieved through the introduction of the electrochemical deoxidation technique, which used molten  $\text{CaCl}_2$  and displayed feasibility of producing oxygen-free titanium<sup>5</sup>.

Currently, Ono and Suzuki are developing a commercial process for titanium production by calciothermic reduction of  $\text{TiO}_2$  in molten  $\text{CaCl}_2$ <sup>8-9</sup>. Features and differences between the FFC process<sup>2</sup> and OS process<sup>8</sup> are under discussion. The application of electronically mediated reaction (EMR)<sup>10</sup> to titanium reduction process is also under progress<sup>11</sup>. This method has the potential for preventing accumulation of impurities into metal deposits<sup>12</sup>, and can increase energy efficiency when combined with conventional molten salt electrolysis (MSE) of  $\text{CaCl}_2$  for calcium alloy reductant production.

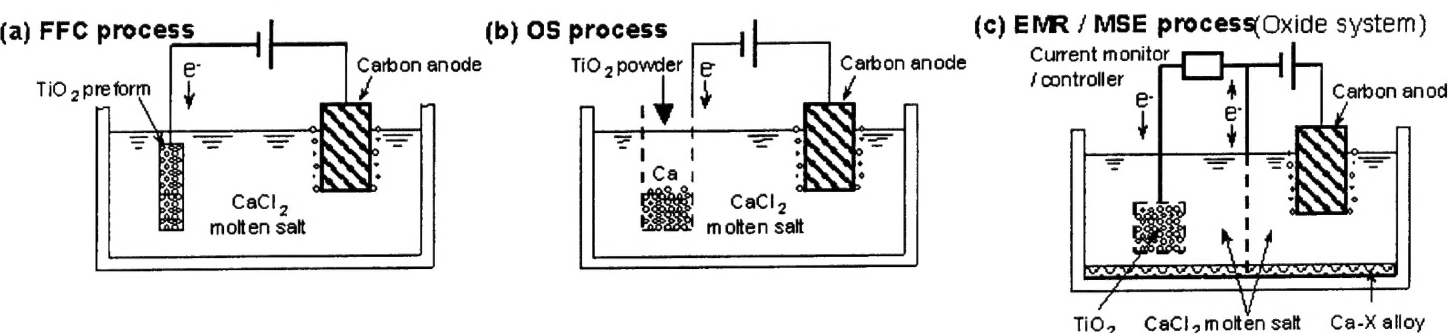


Figure 1. Various reduction processes of  $\text{TiO}_2$  in molten  $\text{CaCl}_2$ .

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## RAMAN SPECTROSCOPIC STUDIES IN MELTS AND SLAGS UP TO 2200K

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Raman spectroscopy is used for studying the structural properties of molten metal halides and molten metal oxides in the temperature range 500-2200K. Optical furnaces and macro-Raman techniques as well as heated microscope stage and micro-Raman techniques are used for measuring spectra of glass forming metal halide melts at temperatures below 1200K. A new high temperature Raman set up has been developed and build for Raman spectroscopic measurements of ceramic melt oxide materials at temperatures up to 2200K. Contain less and self supporting methods for handling the highly corrosive oxide melts and a CW carbon dioxide laser (10.6microns /240wats)for heating the samples were used for the high temperature measurements.

Glassy, super cooled and molten zinc halides have been studied over a broad temperature range 77-1125K in an effort to follow in detail the structural changes caused by temperature variation. A comparison between the spectra features of crystals, glasses and melts have revealed the network structure of the glasses and melts consists of zinc halide tetrahedra bound to each other by apex- and edge-bridged halides. The substructure of the glass/melt is formed by mixing a variety of tetrahedra participating in "open", "cluster" and "chain" networks which are bound to each other by bridged halides. The boundaries of the substructures involve neutral or charged terminal halide bonds with zinc in an average three-fold coordination. Temperature rise breaks-up the substructure to smaller fragments, increases the number of terminal bonds and rearranges the apex and edge bridging network.

Molten mixtures involving oxides of alumina, calcia and silica have been studied as glasses and melts at different compositions and temperatures from room to 2200K. Tetrahedra formed in the glass/melt are bound by apex-bridged oxygens but increasing calcia content leads to the formation of aluminium -oxygen terminal bonds.

## INTERFACIAL PHASE TRANSITIONS IN COULOMB LIQUIDS

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In comparison with simple van der Waals type liquids, our knowledge of the interfacial properties of fluids dominated by Coulomb or screened Coulomb interactions – molten salts and liquid metals – is rather poor. This includes their microscopic and electronic structure and, in particular, their thermodynamic interfacial properties. This applies to both the liquid/vapour and the liquid/solid interface and is even less understood for the case of confined geometries or electrified interfaces. The "double layer" problem in an ionic electrolyte is not yet solved.

In this contribution we report and discuss new experimental results on two types of interfacial phase transitions in Coulomb liquids:

- $\alpha$ ) Wetting transitions in a metal-molten salt mixture (K-KCl) at the fluid/wall interface
- $\beta$ ) Surface freezing transitions in binary liquid alloys (Ga-Bi, Ga-Pb) at the fluid/vapour interface

**"Slow relaxing entities in molten salts, fast relaxing entities in glassy salts, and the crossover between them".**

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 Arizona State University, Tempe, AZ 85287

Lithium ions move rapidly relative to the anion sub-lattice in  $\text{LiAlCl}_4$  and  $\text{LiAlCl}_4 + \text{LiAlI}_4$  eutectic melts. However they move slowly, relative to the anion sub-lattice in  $\text{LiAlCl}_4 + \text{BAI}_4$  solutions, where B stands for "Big cation". B can be a tetraalkyl ammonium cation or any one of the imidazole-based or pyridine-based cations in popular use. The reason is to do with the trapping of the lithium ion in the solutions of large cations which is deleterious to their use as battery electrolytes, which their high conductivities would seem to support. Before discussing the origin of the "trapped" vs "free" status of such small cations in ionic liquids, we will review new work on different families of ionic liquids. We will use the classical Walden product to assess the effects of different anionic and cationic contributions to the differences in "fragility" which we observe in ionic liquids

As part of the discussion on the cation detrapping problem, the matter of such different time scales for different chemical entity motions in liquids will be generalized so as to provide an improved basis for understanding fast ion conducting glasses. These may be encountered when  $T_g$  for the solution rises above ambient. The generalization will involve the definition of a second fictive temperature,  $T_{\text{chem}}$ , for those glasses in which chemical order fluctuations have longer time scales than the viscosity-based Maxwell relaxation time  $\tau = \eta/G_\infty$  where  $G_\infty$  is the high frequency shear modulus and  $\eta$  is the shear viscosity.

## **ROOM TEMPERATURE IONIC LIQUIDS AND REDOX MELTS FOR LIGHT EMITTING DIODES AND PHOTOVOLTAIC CELLS**

M Graetzel *EPFL, Lausanne, Switzerland*

The lecture will describe new electrochemical applications of room temperature ionic liquids. In particular results obtained with dye sensitized nanocrystalline solar cells will be presented. Liquid imidazolium iodide salts exhibit very attractive properties for use as redox electrolytes in these novel photovoltaic devices. Based on their excellent thermal and photo- stability ionic liquids are particularly suited for outdoor applications.

Despite the high viscosity of these salts, a linear dependance of the photocurrent on light intensity up to full AM 1.5 sunlight, excellent fill factors exceeding 0.7 and overall conversion efficiencies of 6.5 % have now been reached with such cells. The reasons for these surprising observations will be analysed and strategies to further increase the photovoltaic performance of these highly stable devices will be presented. Other applications of such ionic liquids, e.g in electrochromic display devices will also be discussed.



**KEYNOTE**

**LECTURES**

## KEYNOTE LECTURES

- K1     **Ionic Liquids for Materials Electrosynthesis**  
F Endres *University of Karlsruhe, Germany*
- K2     **Materials Synthesis in Room Temperature Ionic Liquid**  
H C De Long *Naval Research Laboratory, Washington, USA*
- K3     **Microscopic Dynamics of Liquid Aluminium Oxide**  
D L Price *CNRS-CRMHT, Orleans, France*
- K4     **High Temperature <sup>19</sup>F NMR Spectroscopy in Molten Lanthanide Fluorides**  
C Bessada *CNRS-CRMHT, France*
- K5     **Surface Tension of the Liquid-Vapour Interface of Molten Salts**  
A Aguado *University of Oxford, UK*
- K6     **Phase Formation at the Electrode-Ionic Liquid Interface**  
C Zell *University of Karlsruhe, Germany*
- K7     **Specific Heat Capacities of Common Room Temperature Ionic Liquids: An Examination of the Potential for using Ionic Liquids as Thermal Fluids**  
J D Holbrey *University of Alabama, USA*
- K8     **A New Look at Molten Salt Oxidation**  
T R Griffiths *University of Leeds, UK*
- K9     **Changing Ionic Liquid Behaviour with Supercritical CO<sub>2</sub>**  
J F Brennecke *University of Notre Dame, USA*
- K10    **Battery Applications of Ambient-Temperature and Low-Temperature Molten Salts**  
P C Trulove *Airforce Office of Scientific Research, USA*
- K11    **Cobalt and Titanium-based Protective Coatings for the Molten Carbonate Fuel Cell Nickel Cathode**  
L Mendoza *ENSC de Paris, France*
- K12    **Simulations of Imidazolium Ionic Liquids**  
R M Lynden-Bell *The Queen's University of Belfast, UK*
- K13    **Experimental Studies of Local Structure and Solvation in Room Temperature Ionic Melts**  
C Hardacre *The Queen's University of Belfast, UK*
- K14    **Polarity of Ionic Liquids**  
T Welton *Imperial College, UK*
- K15    **Challenges and Opportunities in the Use of Ionic Liquids: Separations, Extractions and the Choice of Ionic Liquid**  
R D Rogers *University of Alabama, USA*

## IONIC LIQUIDS: SOLVENTS FOR THE ELECTROSYNTHESIS OF METALS AND SEMICONDUCTORS

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In a wider sense ionic liquids are molten salts with a melting point below 100°C<sup>[1]</sup>. They are based on different organic and/or inorganic cations and anions and have specific ionic conductivities between approximately  $10^{-3}$ – $10^{-1}$  ( $\Omega\text{ cm}$ )<sup>-1</sup>. Two systems, that are pretty interesting for electrochemical purposes, are 1-Butyl-3-ethylimidazoliumhexafluorophosphate ([BMIm]PF<sub>6</sub>) and 1-Butyl-3-methylimidazolium bis-(trifluoromethyl-sulfonyl)imide ([BMIm]BTA). Both liquids are easy to prepare and water contents below 50 ppm can easily be achieved. Furthermore, on Au(111) they have electrochemical windows of a little more than 4 Volt: at the cathodic limit an undefined reduction of the organic cation sets in, gold oxidation occurs at the anodic limit. In comparison to the widely employed aqueous solutions the electrochemical windows of these 2 systems are wider by a factor of 3. Another interesting feature is, that these liquids have extraordinarily low vapour pressures and a high chemical stability: for example, [BMIm]BTA can be heated under air up to 350°C without decomposition. It could be shown at the examples of Ag-, Cu-, Ni- and Al-electrodeposition, that ionic liquids are well suited to study the nanoscale processes of electrochemical phase formation, in part even with atomic resolution. In more recent studies the focus was set on the initial stages of the electrodeposition of germanium on Au(111). Germanium quantum dots made by UHV techniques, for example, are known to show size dependent photoluminescence. With GeI<sub>4</sub>, GeBr<sub>4</sub> and GeCl<sub>4</sub> in a wider sense both underpotential (UPD) and overpotential electrodeposition (OPD) is observed. In the "UPD" regime 2D islands grow that close to an approximately 300 pm high monolayer with clearly metallic behaviour, as we could prove with in situ I/U tunneling spectroscopy. In the OPD regime nanoclusters form from GeI<sub>4</sub> first, but they transform in a complex annealing process into Ge(111) bilayers<sup>[2]</sup> on the time scale of about 1 hour. From GeBr<sub>4</sub> and GeCl<sub>4</sub> nanoclusters form in the OPD regime, too, in the case of GeCl<sub>4</sub> these clusters are stable for days – even during probing with the STM tip – whereas with GeBr<sub>4</sub> a transformation into Ge(111) bilayers could partly be observed<sup>[3,4]</sup>. In situ I/U tunneling spectroscopy shows that a Ge-layer with a thickness of several hundreds of nanometers has a symmetric band gap of  $0.7 \pm 0.1$  eV. This band gap is also obtained for nanoclusters with a height of 10 nm, which is within the limits of error in good agreement with the band gap of 0.67 eV for bulk, microcrystalline germanium at 300K. Apart from germanium electrodeposition such ionic liquids are also very interesting for the investigation of Ti- and Si electrodeposition as well as for the electrodeposition of compound semiconductors like GaP, GaAs and ZnTe, that can hardly be obtained from aqueous or organic solutions. Thus, ionic liquids are promising solvents for electrochemical nanotechnology and they will presumably gain a great interest for such purposes.

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## MATERIALS SYNTHESIS IN ROOM TEMPERATURE IONIC LIQUID

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Ionic liquids can serve as both the medium for the synthesis of various materials and as an integral part of the material formed. Ionic liquids make excellent solvents due their non-aqueous, but ionic nature. A number of organic preparations have been successfully performed in these non-complexing liquids. The advantage is the tunable nature of these ionic liquids to act as the appropriate solvent for the reaction desired. Another method is to use the ionic liquid as part of the reaction or incorporate it into the material. Electrodeposition from these molten salts has been greatly facilitated using these ionic liquids. It has allowed for the synthesis of non-equilibrium alloys, where the ionic liquid takes an active part in the alloy formed. Another advantage has been access to metal deposits that are difficult or impossible to form by other techniques. Examples are transition metal-aluminum alloys and aluminum itself. Finally, these ionic liquids can be incorporated into materials as a composite. Examples are incorporation of the ionic liquid into a polymer matrix with or without an active metal for use as a gel electrolyte, and intercalation of the ionic liquid into the galleries of layered materials either with or without other compounds.

The objectives of the nanocomposite research program are to evaluate, and exploit tri-alkyl-imidazolium-based ionic liquids as novel, thermally stable treatments for layered-silicates and graphite for the purpose of preparing high quality polymer nanocomposites. Initial work has demonstrated the superior thermal stability of trialkylimidazolium treated layered-silicates (montmorillonite (MMT) and fluorinated synthetic mica (FSM)). For example, the onset of thermal decomposition of the hexadecyl-functionalized dimethylimidazolium montmorillonite (DHHDIM-MMT) is over 100°C higher than MMT treated with standard tetraalkylammonium salts. In addition, the DHHDIM-MMT has shown excellent compatibility with polyamide-6 (PA-6), and hence forms high quality PA-6/MMT nanocomposites. The DMHDIM-MMT also forms good quality mixed intercalated and exfoliated nanocomposites with polystyrene. We have also recently been the first to successfully prepare nanocomposites with polyethyleneterephthalate (PET, m.p. 290°C) using conventional extrusion and the hexadecyl-functionalized dimethylimidazolium. A variety of techniques are being used to characterize these novel layered-silicates and nanocomposites; these range from TEM, XRD, TGA/DSC, and NMR.

## MICROSCOPIC DYNAMICS OF LIQUID ALUMINUM OXIDE

D. L. Price<sup>\*1,2</sup>, H. Sinn,<sup>3</sup> B. Glorieux,<sup>1</sup> L. Hennet,<sup>2</sup> A. Alatas,<sup>3</sup> M. Hu,<sup>3</sup> E. E. Alp,<sup>3</sup> J. Bermejo,<sup>4</sup> and M.-L. Saboungi<sup>1,5</sup>

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Despite some recent breakthroughs in the investigation of liquid refractory oxides, their dynamics remain largely uncharted territory due to their high temperatures and extremely corrosive nature. In this talk we present results for collective excitations in liquid aluminium oxide at temperatures in the range 2000-2800°C, obtained by combining a containerless sample environment with inelastic x-ray scattering. With this technique it is possible to "close the gap" that existed previously between the light scattering and neutron scattering domains. The excitation spectra show a well defined triplet structure out to wave vectors  $Q$  of 6 nm<sup>-1</sup> and a single quasielastic peak at higher  $Q$ . The frequencies and widths of the Brillouin peaks exhibit a  $Q$  dependence that follows the hydrodynamic theory but with widths considerably below the hydrodynamic values. The widths of the central Rayleigh line are several orders of magnitude below the hydrodynamic prediction and reflect the microscopic structure of the liquid. Our results open up a new domain in the dynamics of ionic liquids that challenges existing theories.

\*Work supported by the CNRS, the Contract "XI<sup>ème</sup> plan Etat / Région Centre" and by the Office of Science, US Dept. of Energy, under Contract W-31-109-ENG-38.

## HIGH TEMPERATURE $^{19}\text{F}$ NMR SPECTROSCOPY IN MOLTEN LANTHANIDE FLUORIDES

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Lanthanide fluorides are well known for their wide range of technological applications : solids as materials for electrodes, solid states lasers or superionic conductors, or molten in electrolytic processes for metal production or in nuclear wastes recycling by Pyrochemical separation processes. Different structural information has been collected on molten lanthanides halides mixtures by Raman, XRD, neutrons or MD, and the existence of octahedral coordination  $(\text{MX}_6)^{3-}$  with and without bridging halide ions have been reported depending on the composition.

Even if the Ln ions are chemically very similar and their complexes considered as isostructural, due to the shielding of the 4f electrons each of these  $\text{Ln}^{\text{III}}$  ions has its own characteristic effect on the NMR parameters of nuclei in its proximity. In solids, the hyperfine coupling between nucleus and  $\bar{e}$  gives rise to important shift and strong broadening that can make the signals unobservable. In solutions, the induced shifts and relaxation enhancements of lanthanides reagents are used extensively in MRI or catalysis, improving the separation of overlapping signals and thus the resolution. In molten salts, in addition to the paramagnetism, we have to deal with the high temperatures, and the experimental difficulties encountered with molten fluorides...

$\text{La}^{\text{III}}$  and  $\text{Y}^{\text{III}}$  having no unpaired electron are diamagnetic. Using their analogy with the other lanthanides a first NMR study have been performed on molten mixtures  $\text{YF}_3\text{-LiF}$  and  $\text{LaF}_3\text{-LiF}$  at temperatures up to  $1000^\circ\text{C}$ , by means of  $^{19}\text{F}$  and  $^7\text{Li}$  observations. The evolution of the  $^{19}\text{F}$  chemical shifts over the whole composition range, confirms the existence of octahedral complexes in the melts and the structural evolution with the composition. The NMR parameters obtained are then compared with  $^{19}\text{F}$  spectra obtained for  $\text{NdF}_3\text{-LiF}$  system.



## Surface Tension of the Liquid-Vapour Interface of Molten Salts.

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Molecular dynamics simulations in the NVT ensemble are used to calculate the surface tension  $\gamma$  and study the structural properties of the liquid-vapour interface of simple molten salts KI, LiCl, KCl and LiCl-KCl binary mixtures. KI will be taken as an example to discuss the importance that several terms in the interionic potential and simulation models have on the calculated surface tension. Specifically, we will show that: (a) an Ewald summation of dispersion interactions is necessary to avoid substantial truncation effects; (b) inclusion of polarization interactions tends to decrease  $\gamma$  by significant amounts, and improves the agreement with experiment; (c) varying the width of the simulation slab has not any effect on the calculated surface tensions; (d) sizable finite size corrections emerge upon increasing the lateral dimensions.

A comparison of the structure of LiCl and KCl interfaces allows us to discuss the relevance of size asymmetry effects on interfacial properties. These effects are apparent in the structure of the LiCl interface, but only when a description of polarization interactions is included in the potential model. Polarization facilitates the formation of a displacement dipole moment across the interface by allowing an opposing electronic dipole moment of approximately the same magnitude, so that the total dipole moment is always small and thus not unfavorable from an electrostatic point of view.

The study of the binary mixtures shows that the surface tension is relatively insensitive to the specific LiCl concentration for a broad range of compositions. This is explained by potassium segregation towards the surface. For all the systems studied, the local ion coordination number reduces to 50 % of its bulk value only when the ion density has reduced to less than 5 % of its bulk value, showing the importance of clustering effects in this kind of interface.

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## PHASE FORMATION AT THE ELECTRODE – IONIC LIQUID INTERFACE

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The electrodeposition of metals, nonmetals and compounds from molten salts is very important technologically. Despite intensive research of these processes for several decades, little is known about the initial stages of phase formation and growth at the electrode/ionic liquid interface on an atomic or nanometre scale. This became possible only recently by *in situ* scanning probe microscopy (SPM) in the environment of ionic electrolytes.

In this report we give a brief survey of recent STM and STS studies of electrodeposition of transition metals, alloys, and semiconductors from room temperature molten salts. The following topics will be addressed:

- 2D phase formation of Co and Ni and surface alloying;
- 3D cluster growth at the electrode interface
- Nanometre size Al-alloy cluster formation and variation of their electronic structure probed *in situ* by STS
- Thickness induced M-NM transition in ultra-thin electrodeposited Ge-films

Specific heat capacities of common room temperature ionic liquids:  
an examination of the potential for using ionic liquids as thermal fluids.

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Ionic liquids (ILs) are potentially excellent fluids for use in a wide range of engineering and materials applications. Negligible vapor pressure is exhibited by many ILs over a wide temperature range and provides liquid stability over a wide range of conditions. However, the absence of specific heat capacity data for ILs in the literature is a significant hurdle to the assessment and design of IL chemical reactors and heat transfer systems.

The heat capacities for a range of 1-alkyl-3-methylimidazolium ILs containing either a common cation, or common anion, have been measured by modulated DSC, in order to determine both the magnitude of the heat capacities of ILs (with relevance to engineering and thermal fluids) and the effect of differing structural group-contributions (which provides data on cation-anion interactions). For all the ionic liquids in this study, the specific heat capacity was determined to be between 1.0-2.1 J/gK at 298 K, and increased linearly with temperature in the liquid region. The magnitude of the heat capacity increases with increasing anion-cation interactions in the IL (i.e., hydrogen-bonding) following the order  $[\text{NTf}_2]^- \sim [\text{PF}_6]^- < [\text{BF}_4]^- < \text{Cl}^-$ . The results, when combined with data on liquidus ranges, thermal expansion coefficients, density, thermal stability, materials compatibility, and cost etc., can be compared with the properties of common organic thermal fluids and indicate that ionic liquids could be considered as candidates for heat transfer applications.

## A NEW LOOK AT MOLTEN SALT OXIDATION

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Molten Salt Oxidation, MSO, is conventionally a thermal, non-flame process that destroys completely many organic compounds and simultaneously retains all other products, both non-oxidisable and non-volatile inorganic species, in a molten carbonate. The waste is delivered, with an air stream, into the salt bath and the hydrocarbons are therein converted to an off-gas of carbon dioxide, steam and nitrogen.

MSO is not a new concept, having been examined as a possible method for processing nuclear fuels by the Atomic Energy Commission in the USA in the 1950's. Other applications of MSO were soon envisioned and tested, including the destruction of hazardous waste, of propellants and explosives, and for metal recovery and volume reduction of radioactive waste. Although successful, these processes were not taken beyond pilot plant scale, as established methods then available were acceptable.

In recent years emissions levels and the old disposal methods are now of international concern. Combustion produces ash and unacceptable emissions and the combustion of organic wastes containing chlorinated plastics is seen as source of dioxins. Burial of waste can give concern for the possible future contamination of ground water. The disposal of the large tonnage of tyre waste generated worldwide is becoming an increasing environmental and economic problem. In the EU, the burial of old tires will soon be prohibited. New methods are therefore now needed.

The major advantages of MSO include:

- Good retention of metal oxides or inorganic salts in the molten carbonate
- The entrained salts in the cooled off-gases are easily collected and discharged as a residue.
- Elements that form acid gases (F, Cl, Br, I, S, P, N etc.) react with the alkaline melt to form the corresponding inorganic salt, and thus are retained in the melt.
- The large thermal mass of the molten salt provides a stable heat transfer medium that resists thermal surges, and the system is thus able to tolerate rapid process fluctuations.
- Flame-outs are completely avoided, since MSO is a non-flame process.
- Less off-gas is generated than by incineration, since it does not require supplemental fuel to sustain a flame, and hence has economic advantages.
- The MSO system also operates at much lower temperatures than flame combustion temperatures and thus avoids the emissions products formed at high temperatures, particularly furans and dioxins.
- Low cost of materials.

In the last decade over \$40M were spent in the USA re-examining MSO but support was recently terminated, due to the incomplete and often slow oxidation of common materials such as a paper. The literature on the oxidation of various wastes, if it attempts to explain the mechanism of oxidation, refers to the catalytic role of carbonate, justified on the basis that oxidation occurs at a lower temperature than combustion. To improve reaction rates experiments were consequently proposed and undertaken with traditional catalyst promoters, transition metal oxides, added as potential catalysts. The amounts needed to produce a slight improvement were around 40% but then the systems were more viscous. Our new approach to MSO recognises that the role of carbonate is not as a catalyst. The action of the molten carbonate is to dissolve chemically some of the oxygen bubbling through the melt. Further, since we had shown that the active species formed are peroxide and superoxide, the latter predominating, we predicted and subsequently showed that a small amount of nitrate would act as a catalyst, increasing the concentration of peroxide and superoxide in the melt. Experiments with paper, various plastics and scrap rubber showed that these materials would now be completely oxidised, and more quickly. In the case of rubber, the rubber had to first be treated to de-vulcanise it, for which we developed a new procedure.

The background to MSO will be briefly reviewed and our novel developments and results then described. These show that MSO is now a resurrected technique, capable of oxidising safely and completely wastes that soon can no longer be burned or buried: hazardous wastes containing pathogens can be destroyed on site and cotton and paper wipes containing low level radioactivity are contained in small volumes.

## Changing Ionic Liquid Behaviour with Supercritical CO<sub>2</sub>

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Previously, we have shown that ionic liquids (ILs), including the dialkylimidazolium salts, have a high capacity for carbon dioxide (Blanchard et al., *J. Phys. Chem. B*, **105**, **2001**, 2437). One can take advantage of this property to perform gas separations using ionic liquids if the other components in the mixture are gases that do not have high solubility in the organic salts (such as nitrogen, oxygen, methane, etc.) (Anthony et al., *J. Phys. Chem. B*, in press, **2002**). We have also shown that supercritical CO<sub>2</sub> can be used to extract organic components out of ionic liquid mixtures, such as one might encounter when performing reactions in these salts (Blanchard et al., *Nature*, **399**, **1999**, 28; Blanchard and Brennecke, *Ind. Eng. Chem. Res.*, **40**(1), **2001**, 287). Interestingly, there is no measurable IL in the CO<sub>2</sub>-rich extract. In performing these extractions, significant amounts of CO<sub>2</sub> will dissolve in the ionic liquid mixtures. In this presentation, we will show results of how the presence of CO<sub>2</sub> changes the solvent strength of ionic liquids. Moreover, we investigate how the presence of CO<sub>2</sub> dissolved in mixtures of ionic liquids and organic compounds (or water) influences the phase behaviour.

Specifically, we use phenol blue and pyrene-3-carboxaldehyde as solvatochromic probes to establish the presence of specific interactions between ILs and polar solutes. We find that the solvent strength of the imidazolium based ILs is due to both hydrogen bonding and nonspecific interactions and, overall, is similar to that of primary alcohols. The effect of changing the anion (PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) was quite small. . The solvent strength of the IL does decrease upon addition of CO<sub>2</sub> but the decrease is rather small until large amounts of CO<sub>2</sub> have dissolved. This is in contrast to mixtures of CO<sub>2</sub> with polar organic solvents, where relatively small amounts of CO<sub>2</sub> cause a significant decrease in the solvent strength.

When CO<sub>2</sub> pressure is applied to mixtures of ILs and organics or IL and water, the CO<sub>2</sub> uptake depends, to a large extent, on the amount of IL present in the mixtures. Most interestingly, we find that when the IL is the minor component in the mixture, the application of CO<sub>2</sub> pressure actually caused the formation of an additional liquid phase, which contains most of the IL in the system. This is easily understood for the case of the IL/organic mixtures. The phase split occurs because the CO<sub>2</sub> expands the organic compound (such as methanol), reducing its solvent power, which effectively forces the IL out of solution. The process is analogous to the separation of heavy hydrocarbons from lubrication or other petroleum oils using CO<sub>2</sub> except that with ILs there is none of the "precipitated" liquid in the CO<sub>2</sub>-rich phase. Thus, we have shown that it is possible to use CO<sub>2</sub> to separate ILs from organic or aqueous mixtures without having to extract all of the volatile components, which makes this a complementary technique to supercritical extraction. It also points out, though, that the solvent strength of IL/organic mixtures is dramatically altered when CO<sub>2</sub> pressure is applied, which can even result in the formation of additional, perhaps unwanted, liquid phases.

## BATTERY APPLICATIONS OF AMBIENT-TEMPERATURE MOLTEN SALTS

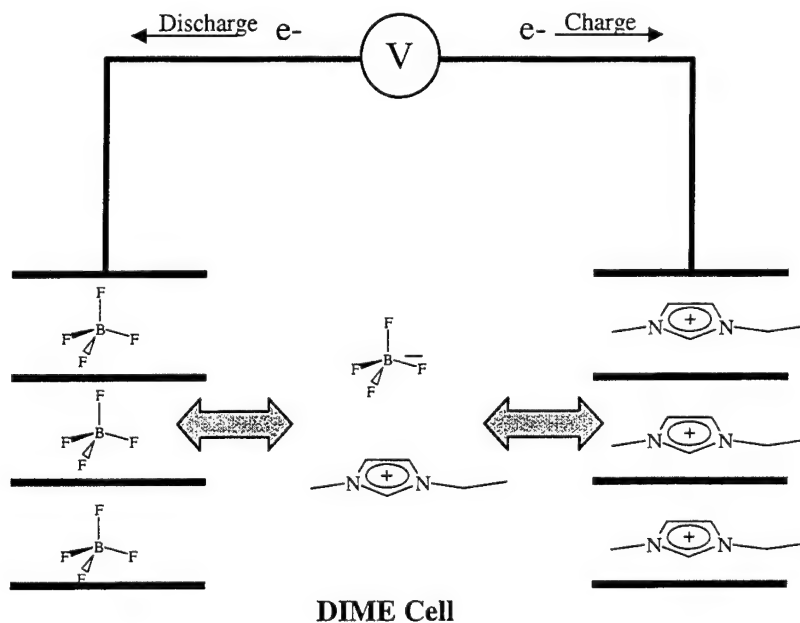
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Much of the original impetus for the development of room-temperature molten salts resulted from their application as electrolytes for high-energy density batteries. The majority of this effort focused on the dialkylimidazolium chloroaluminate ionic liquids. A great deal of work was done studying a wide variety of anode and cathode systems. However, it appears that none of this research has been transitioned into a commercial battery system. Consequently, investigations into the battery applications of chloroaluminate ionic liquids have dwindled significantly in recent years. The recent development of air and water stable room-temperature molten salts has lead to an explosion of research into their application in a wide variety of areas. Nonetheless, a relatively small number of studies have focused on their use in battery systems. Some effort has been extended characterizing the electrolyte properties of these new molten salts, and they have been studied for use in polymer-gel electrolytes. A limited amount of work has gone into studying their use as electrolytes for lithium-ion "rocking-chair" type batteries, and they have been investigated for use in super capacitors. In addition, these air and water stable molten salts have been investigated for their application in Dual Intercalating Molten Electrolyte (DIME) battery systems. This novel concept utilizes two graphite electrodes and the molten salt anion and cation as electrochemical intercalates. Significant work in the DIME systems has gone into designing stable anion and cation intercalates, as well as optimizing the graphitic electrodes.





## COBALT AND TITANIUM-BASED PROTECTIVE COATINGS FOR THE MOLTEN CARBONATE FUEL CELL NICKEL CATHODE

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Significant advances have been realised in the last years on the molten carbonate fuel cell technology (MCFC), in particular, in the USA and Europe (Germany and Italy). A rapid overview is given on the principle, materials, problematic and prototypes of the molten carbonate fuel cell. Nevertheless, the understanding and improvement of the MCFC system and materials is still an important trend in order to commercialise this electrochemical device.

The state-of-the-art molten carbonate fuel cell (MCFC) nickel cathode, *in situ* oxidised and lithiated:  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ , presents a relatively high solubility in the electrolyte which can provoke the formation of metallic nickel and short-circuit between the anode and the cathode. Alternative electrode materials should be more stable in the carbonate medium and allow to obtain electrical performance as good as  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ .  $\text{LiCoO}_2$  and  $\text{Li}_2\text{TiO}_3$  appear as good candidates because of their low solubility under the standard MCFC conditions ( $\text{O}_2/\text{CO}_2$  (70/30) atmosphere, but their conductivity is lower than that of lithiated NiO. The interest of well-controlled  $\text{LiCoO}_2$  or  $\text{Li}_2\text{TiO}_3$  layers on a nickel or nickel oxide substrate, combining the good properties of NiO with the protective role of these oxides, is a crucial.

Electrochemical deposition, a cheap and low temperature technique, has been used to produce thin and homogeneous layers of  $\text{Co}_3\text{O}_4$  on nickel samples. Sputtering was used to elaborate good quality  $\text{TiO}_2$  thin layers on nickel samples. These oxides were transformed in  $\text{LiCoO}_2$  and  $\text{Li}_2\text{TiO}_3$ , respectively, by exposure to the molten carbonate.

These deposits were directly and after exposure to the molten salt characterised by cyclic voltammetry, scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

The methodology and techniques presented can be extended to several kinds of materials, in particular ultra thin coatings with complex composition. A new insight in the control and understanding of the cathode (and by extension to the anode and bipolar plate materials, separating each elementary cell from the other) is one of the key problems in order to develop more reliable MCFC systems.

## SIMULATIONS OF IMIDAZOLIUM IONIC LIQUIDS

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Simulations of liquids such as water have greatly increased our understanding of the structure and dynamics on the molecular scale and how these are related to experimentally observable quantities. Simulations of room temperature ionic liquids are in their infancy, but are already giving a clear picture of some properties of these liquids. In this contribution we shall outline results concerning the local environment around the imidazolium ion and around various small molecules in dilute solution in [dmim][Cl]. The average local environment around the solute is then used to interpret the energetics and chemical potential values that we calculate. Finally some results concerning the structure of the liquid-vapour surfaces of some neat ionic liquids and water-ionic liquid mixtures will be given.

## **Experimental Studies of Local Structure and Solvation in Room Temperature Ionic Melts**

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The structure of ionic liquids has been examined using neutron and X-ray diffraction. This talk will summarise the work performed on examining the local structure of a range of imidazolium based ionic liquids including both short and long alkyl chain length materials. The liquid structure will be compared with that found in the solid state and the close similarity between the structure highlighted. Preliminary results will also be presented on the effect of solutes such as benzene and water dissolved in dimethylimidazolium based ionic liquids. Using protiated and deuteriated forms of both the ionic liquids and the solutes, it is possible to isolate the solute-solute, solute-solvent and solvent-solvent interactions. Some crystal structures have also been obtained. Of particular interest is the structure of benzene in dimethylimidazolium hexafluorophosphate.

## IONIC LIQUID POLARITY

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**Abstract**

Ionic liquids are becoming increasingly popular as solvents for a wide range of applications in synthesis and catalysis.<sup>1</sup> Although estimates vary, there is no doubt that the number of possible combinations of anions and cations that will give rise to ionic liquids is vast. This potential for synthetic variation has led to ionic liquids being called "Designer Solvents".<sup>2</sup> However, in order to achieve this aim it is necessary to know exactly what is being designed, which parameters are flexible and which are fixed. Further to this, although the large number of potential ionic liquids provides synthetic flexibility, it also presents a problem, in that it is not possible to make every possible combination of ions and measure its properties. Hence there is a need to generate a predictive capacity. Finally, it is also necessary to be able to compare ionic liquids to the molecular solvents that they may one day replace.

The key characteristics of a liquid that is to be used as a solvent are those that determine how it will interact with potential solutes. For molecular solvents, this is most commonly recorded as the polarity of the pure liquid, as expressed through its dielectric constant. The inability of this scale to provide adequate correlations with much experimental data has led to the use of empirically derived measurements of solvent properties.<sup>3</sup> A range of ionic liquids has been investigated using the Kamlet-Taft parameters<sup>4</sup>  $\alpha$ ,  $\beta$ , and  $\pi^*$ . It was found that  $\pi^*$  is high for all of the ionic liquids studied and varies with both anion and cation,  $\alpha$  is generally moderate and depends mainly on the cation, and  $\beta$  is modest and depends mainly on the anion. The results are compared to investigations of the rates and product selectivities of some simple chemical reactions.

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Challenges and opportunities in the use of ionic liquids:  
separations, extractions, and the choice of ionic liquid.

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Chemical transformations or syntheses hold a pivotal role in chemical processes, however, product isolation through extraction and separations techniques are of fundamental importance in order to effectively utilize the chemical transformation steps. With the general move towards green chemical practice, processes are being re-evaluated in order to increase overall efficiency by elimination of waste, side products, and expensive reagents and solvents. Among these directors is the desire to reduce reliance on VOCs, especially halogenated organic solvents.

Techniques and approaches to clean separations and product isolation with regard to chemical reactions and processing in, or using, ionic liquid (IL) systems include precipitation, secondary extraction, sc-CO<sub>2</sub>, pH switching, distillation, IL-gas separations, membrane separations, and dissolution and washing of ionic liquids. Developments in these fields come from an understanding of ILs and their solvation and solvent properties.

The requirements and potential benefits of using ionic liquids will be discussed in the context of chemical, nuclear, and other separations processes. Descriptors for solvent-solute interactions of common organic solutes in ionic liquid/aqueous and ionic liquid/organic systems have been developed and can provide valuable data to enable improved performance in extractions through understanding and design of the liquid extraction system.

Practical examples in the context of polymerizations, bio-product processing, and metal and radiochemical separations using ILs, including polymer synthesis and dissolution, cellulose dissolution and regeneration, actinide extraction and partitioning, and salt-salt separations will be presented.





**CONTRIBUTED**

**ORALS**

## CONTRIBUTED ORALS

- C1 **Thermochemistry of the Vapour of the Corrosion Systems  $\text{NaX-TmX}_3 + \text{Al}_2\text{O}_3$  ( $\text{X}=\text{Br}, \text{I}$ )**  
T Markus *Research Centre Jülich, Germany*
- C2 **Electrochemical Formation of Boride Coatings on Aluminium from the Chloride Melts with Addition of  $\text{B}_4\text{C}$  and  $\text{B}_2\text{O}_3$**   
L A Yolshina\*, O V Belova and V Ya Kudyakova *Urals Branch of RAS, Russia*
- C3 **Chlorine Evolution at High Current Densities in a  $\text{ZnCl}_2\text{-NaCl-KCl}$  Electrolyte**  
S C Lans\*, A van Sandwijk, M A Reuter, J Vandenhaut and E Robert *Delft University of Technology, Netherlands*
- C4 **Silicon Deposition from a Chloride Based Melt**  
E Olsen *SINTEF Materials Technology, Norway*
- C5 **Electrochemical Synthesis of Binary Carbides of Molybdenum and Tungsten in Ionic Melts under excess pressure Carbon Dioxide  $\text{CO}_2$**   
H B Kushhov\*, L M Beroeva and R A Karashaeva *Kabardino-Balkarian State University, Russia*
- C6 **The Chemla Effect in Molten Alkali Nitrates: A Molecular Dynamics Study**  
M C C Ribeiro *Universidade de Sao Paulo, Brazil*
- C7 **Dependence of Thermal Conductivity in Molten Salts on Ionic Mass**  
N Ohtori\*, T Oono, Y Togawa, Y Suzuki and K Takase *Niigata University, Japan*
- C8 **Structure of molten  $\text{PbF}_2$  obtained by EXAFS spectroscopy**  
S Watanabe, R Toyoyoshi, T Sakamoto, Y Okamoto, Y Iwadate, H Akatsuka and H Matsuura\* *Tokyo Institute of Technology, Japan*
- C9 **Visualization of MD Results on Crystallisation of  $\text{MgO}$  from its Melt**  
I Okada\*, Y Utsunomiya, H Uchida, M Aizawa, K Itatani, Y Tamura and F Tanaka *Sophia University, Japan*
- C10 **The Application of the New Model of Electric Double Layer of Electrodes in Molten Salts in the Study of Electrode Reactions in Magnesium and Aluminium Electrolysis**  
A Kiswa *University of Wroclaw, Poland*
- C11 **Applications of Molten Salts for Production of Refractory Metals**  
S A Kuznetsov\*, S V Kuznetsova, V N Bezumov and G N Titov *Institute of Chemistry Kola Science Centre RAS, Russia*
- C12 **Inert Anodes for Aluminium Electrolysis: A New Technology?**  
J Thonstad *Norwegian University of Science and Technology, Norway*

- C13 **Treatment of Molten Salt Wastes by Phosphate Precipitation**  
V A Volkovich\*, T R Griffiths, and R C Thied *University of Manchester, UK*
- C14 **Carbon Electrodeposition Process in Molten Fluorides**  
L Massot\*, P Chamelot, F Bouer and P Taxil  
*CEA/VALRHQ, DEN/DTE/STME, France*
- C15 **Viscosity of Molten Rare Earth Chlorides**  
V Khokhlov\*, A Potapov and Y Sato *Institute of High-Temperature Electrochemistry, Russia*
- C16 **Morphology and Formation Mechanism of Electrodeoxidized Niobium Metal in Molten Chlorides**  
X Y Yan\* and D J Fray *University of Cambridge, UK*
- C17 **Scaling Relationships for Freezing Points of Liquid Ionic Salts**  
L V Woodcock *US Air Force Research Laboratory, USA*
- C18 **Ionic Liquid Crystals: From Discovery up to Present Day**  
T A Mirnaya\* and S V Volkov *Ukrainian Academy of Sciences*
- C19 **Polymerizable Ionic Liquids and their Polymers for Ion Conductive Flexible Matrix**  
H Ohno *Tokyo University of Agriculture and Technology, Japan*
- C20 **Group15 Based Quaternary Salts: The Development of Ionic Liquids with Large Electrochemical Windows**  
A I Bhatt\*, V A Volkovich, I May, D Collison and M E Heterington  
*University of Manchester, UK*
- C21 **Microstructure and Crystallisation History of Molten Salts Decoding by Means of the Homogeneous Regions Borders Models**  
V P Vorob'eva *Buryat Scientific Center, Russia*
- C22 **Molten Salts in Battery Materials**  
A G Ritchie\* and P G Bowles *QinetiQ, UK*
- C23 **New Functionalised Ionic Liquids and their Commercial Availability**  
U Welz-Biermann *Merck, Germany*
- C24 **Low Temperature Melts for Electrodeposition of Metals**  
O I Boiko *Ukrainian Academy of Sciences*
- C25 **Temperature Dependence of Viscosity and Conductivity for Various Room Temperature Ionic Liquids**  
O O Okoturu *Queen Mary University of London, UK*

## THERMOCHEMISTRY OF THE VAPOUR OF THE CORROSION SYSTEMS NaX - TmX<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> (X= Br, I)

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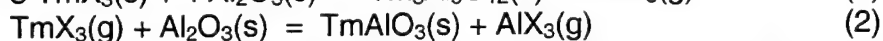
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### 1. Introduction

The vapor of the systems NaX - TmX<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> (X= Br, I) was investigated under equilibrium conditions in the temperature range from 744 to 1134 K by using Knudsen Effusion Mass Spectrometry with a one compartment Knudsen cell. The determination of reliable values for the thermodynamics of corrosion reactions between the salt mixture and solid alumina is the aim of this work. The formation of hetero complexes between salt components and additionally between NaX und AlX<sub>3</sub> (the latter arising from reaction between TmX<sub>3</sub> and alumina) could be observed and the enthalpies and entropies of formation of the hetero complexes were determined. The study of gaseous metal halide complexes is of fundamental interest for the chemistry of coordination compounds. In addition gaseous metal halide complexes are of importance for chemical vapour transport. The potential of enhanced vapour phase material transport by hetero complex formation has been described by Schäfer<sup>[1]</sup>. Chemical vapor transport is of interest for metal halide lamps, chemical vapor deposition, and metallurgical processes. The investigations complement our systematic studies on high temperature lamp chemistry<sup>[2], [3]</sup> and enhancements of metal concentrations by means of hetero complex formation<sup>[4]</sup>.

### 2. Results

Vaporization studies were carried out by Knudsen Effusion Mass Spectrometry. Powder mixtures of NaX, TmX<sub>3</sub> (X= Br, I) and Al<sub>2</sub>O<sub>3</sub> were heated in Knudsen cells made of molybdenum. The vapor species X(g), AlX<sub>3</sub>(g), (AlX<sub>3</sub>)<sub>2</sub>(g), NaX(g), (NaX)<sub>2</sub>(g), TmX<sub>3</sub>(g), (TmX<sub>3</sub>)<sub>2</sub>(g), NaAlX<sub>4</sub>(g), NaTmX<sub>4</sub>(g) and Na<sub>2</sub>TmX<sub>5</sub>(g) were identified in the equilibrium vapor above the sample and the partial pressures of the abundant species were determined. AlX<sub>3</sub> vapor species result from corrosion reactions such as



The solid corrosion products were characterized by XRD and analytical electron microscopy. Thermodynamic data ( $K_p$ ,  $\Delta H$ ,  $\Delta S$ ) describing the stability of the complexes NaAlX<sub>4</sub>(g), NaTmX<sub>4</sub>(g) and Na<sub>2</sub>TmX<sub>5</sub>(g) were determined from the measured partial pressures.

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**Electrochemical formation of boride coatings on aluminum  
from the chloride melts with addition of  $B_4C$  and  $B_2O_3$**

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Boride coatings on aluminum surface have good corrosion and mechanical resistant properties. It is known that solubility of boron in liquid aluminum is 0,22 atomic %. So one can propose that it impossible to produce boride coating on aluminum surface. But boride films on aluminum were obtained with additions both carbide of boron and oxide of boron.

Special investigation it was made to determine solubility of  $B_4C$  and  $B_2O_3$  in wide temperature range in molten eutectic mixture CsCl-NaCl. It was shown that solubility of carbide of boron doesn't depend on the mass of addition and depends only on temperature of experiment. It was shown that solubility of boron oxide is less than it follows from Shreder equation because of evaporation of gaseous boron chloride. The evaporation of boron chloride evidently can significantly decrease the concentration of boron oxide in electrochemical bath.

So it can be used boron carbide for successful formation of boride thin dense extent coatings on aluminum surface. As it was shown by Auger-spectrometry  $AlB_2$  and  $AlB_{12}$  can be formed. at 810 K and at 860 K.

## Chlorine evolution at high current densities in a $\text{ZnCl}_2$ -NaCl-KCl electrolyte

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An experimental study has been carried out on the electrowinning of zinc from a  $\text{ZnCl}_2$ -NaCl-KCl melt. With reference to Zn electrolysis from a sulphate medium a substantial saving on the energy consumption may be achieved since  $\text{ZnCl}_2$  has a considerable lower decomposition potential than  $\text{ZnSO}_4$ . In addition, high current densities can be employed, because of the high conductivity of molten salts and the high solubility of  $\text{ZnCl}_2$  in these electrolytes. The cathodic current density is only limited by the operating temperature and the composition of the electrolyte, because this electrolyte will solidify locally at the cathode due to depletion of  $\text{ZnCl}_2$  at the cathode. The energy consumption is mainly determined by the anodic process, i.e. the production of chlorine. The current densities employed in the experimental work reached  $15 \text{ kA}\cdot\text{m}^{-2}$ , resulting in the formation of large volumes of gas.

Already at relatively small overpotentials, the effective conductivity of the electrolyte is significantly reduced, since the bubbles are non-conductive and reduce the effective electrode area by coverage. At higher overpotentials and high current densities, the number of bubbles adhering to the anode is high, resulting in mutual interactions, such as coalescence. The electrolyte between two parallel plates electrodes consists of a layer with bubbles attached to the electrode and a second layer with rising bubbles. Those two layers together form the gas plume.

The ohmic drop in the electrolyte with vertical plate electrodes is depending on the gas holdup and the geometry of the gas plume, which is determined by bubble attachment, departure, size and rising velocity. The objective of the present work is to model the ohmic drop by studying the gas plume and the effect of electrolyte composition, anode material, temperature, anode height, pressure, as well as bubble size distribution. Electrochemical methods have been used to characterise the electrowinning. In addition, the process was visualised in a see-through furnace and image analysis has been performed to characterise the shape of the plume. A relationship will be developed that relates the ohmic drop to the angle of the gas plume with the electrode, physical properties of the electrolyte, height of the electrode and gas volume fraction, which will be defined by the bubble size distribution.

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The worldwide photovoltaic (PV) industry manufacturing crystalline silicon solar cells for generation of electricity, has experienced a yearly growth in the range 25% – 40% since the early 80's. The PV industry relies on off-spec and scrap silicon from the electronics industry as raw material due to purity requirements. As the growth in the PV-market far exceeds the growth in the market for electronics, a shortage of raw material for the production of solar cells is about to emerge. In order to sustain the market growth, new sources of raw material Si with adequate purity (SoG-Si) has to be developed.

One possible way to produce Si of higher purity than can be accomplished with carbothermic reduction, is by molten salt electrolysis. Molten salt electrolysis can be conducted either by decomposition of the salt itself as in the production of Mg, or by deposition from a compound dissolved in the salt as in the Hall-Heroult production process for Al. Significant effort has been centered around dissolving a Si-containing compound in cryolite or other fluorides. Fluorides has the advantage of being able to dissolve most oxides, and high-purity  $\text{SiO}_2$  is a naturally occurring, moderately priced raw material. The temperature range of molten salt electrolysis is usually far below the melting point of Si, and subsequently this incorporates solid-state precipitation unlike most other molten salt electrolysis processes. As the solid state deposits frequently occur as microcrystals, this introduces the need to extract the deposits from co-deposited bath components. This is difficult in a fluoride environment due to the stability and inertness of the precipitated salt. Chlorides are usually easily soluble in water, but has very limited solubility of oxides. There is, however, one chloride which will dissolve oxides, including  $\text{SiO}_2$ , namely  $\text{CaCl}_2$ .

The chemical system  $\text{CaCl}_2\text{-CaO-SiO}_2$  shows promising results for use in an electrochemical process for the production of Si.  $\text{SiO}_2$  dissolves in the  $\text{CaCl}_2$ -based melt and Si has been deposited by electrolysis. The dissolution of  $\text{SiO}_2$  is enhanced by the addition of CaO. The purity of the deposited Si for the use as SoG-Si is acceptable with regards to B. The deposited Si contained some P which may originate from the CaO used. Other qualities of CaO may contain less P. The dissolution of  $\text{SiO}_2$  in  $\text{CaCl}_2\text{-CaO-}$ containing melts has been studied. The results indicate that  $\text{SiO}_2$  forms a compound with CaO which dissolves in the melt, possibly  $(\text{CaO})_2\cdot\text{SiO}_2$ . Only minor amounts of  $\text{SiO}_2$  was found to dissolve in pure  $\text{CaCl}_2$ , contradictory to previously published data<sup>1</sup>. A patent application<sup>2</sup> has been filed as this is a previously undescribed process for electrochemical production of Si.

<sup>1</sup> P. Stemmermann, H. Pöllmann, N. Jb. Miner. Mh. 1992, H-9, pp 409-431.

<sup>2</sup> International PCT-patent application, PCT/NO02/000195

## Electrochemical synthesis of binary carbides of molybdenum and tungsten in ionic melts under excess pressure carbon dioxide CO<sub>2</sub>

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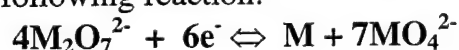
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In the present work are submitted research results of the mechanism of binary carbides of molybdenum and tungsten electrochemical synthesis in oxide (Na<sub>2</sub>WO<sub>4</sub>-WO<sub>3</sub>-MoO<sub>3</sub>) and oxide-chloride KCl-NaCl-Na<sub>2</sub>WO<sub>4</sub>-Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>-Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub> melts under excess pressure oxide of carbon.

For an establishment of the mechanism of electrochemical synthesis we investigated features electrodeposition of tungsten, molybdenum and carbon from oxide and oxide-chloride melts both separately, and in common.

It is established, that in Na<sub>2</sub>WO<sub>4</sub> melt containing oxide WO<sub>3</sub> and MoO<sub>3</sub> takes place the acid-basic interactions.

Tungsten and molybdenum exist in melt as steady Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> and W<sub>2</sub>O<sub>7</sub><sup>2-</sup>-dimeric ions. Electroreduction of Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> and W<sub>2</sub>O<sub>7</sub><sup>2-</sup>-ions proceeds is convertible practically in one stage on the following reaction:

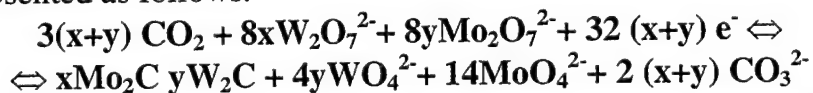


It is shown, that joint multielectronic reduction of Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> and W<sub>2</sub>O<sub>7</sub><sup>2-</sup>-ions is carried out also in one stage in a narrow interval of potentials with reception tungsten- molybdenum alloys.

We are investigated an opportunity the dilution on oxide melt by chlorides of sodium and potassium. It is established that at addition Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub> and Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> in KCl-NaCl melt occurs oxidation-reduction processes to allocation of chlorine. To stabilize ionic forms Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> and W<sub>2</sub>O<sub>7</sub><sup>2-</sup> and the opportunity of joint electroreduction and reception tungsten - molybdenum of alloys is shown.

Creating excess pressure oxide of carbon (up to 15·10<sup>5</sup>Pa) above Na<sub>2</sub>WO<sub>4</sub>-WO<sub>3</sub>-MoO<sub>3</sub> melt and KCl-NaCl-Na<sub>2</sub>WO<sub>4</sub> - Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>-Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub> for the first time in experimental practice joint electroreduction of three components is carried out: tungsten, molybdenum and carbon. That multielectronic process of joint electroreduction dimeric ionic species Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> and W<sub>2</sub>O<sub>7</sub><sup>2-</sup> and oxide of carbon on voltammograms corresponds one wave is amazing. A electrolysis products at potentials of this wave are carbides molybdenum and tungsten of structure (Mo,W)C, (Mo, W)<sub>2</sub>C and firm solutions carbides molybdenum and tungsten.

Total process of electroreduction dimeric ions of tungsten, molybdenum and dioxide carbon can be presented as follows:



It is shown, that the structure of binary carbides depends on concentration of ions Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup>, W<sub>2</sub>O<sub>7</sub><sup>2-</sup>-ions in melt and value of excess pressure oxide of carbon.



## THE CHEMLA EFFECT IN MOLTEN ALKALI NITRATES: A MOLECULAR DYNAMICS STUDY

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The Chemla effect concerns the strong composition dependence of the internal ionic mobilities of cations in mixtures of two molten salts with a common anion, in which the mobility of the large cation can be higher than the small one at low concentrations of the latter.<sup>1</sup> In this work, molecular dynamics (MD) simulations of molten (Li,Cs)NO<sub>3</sub>, (Li,K)NO<sub>3</sub>, (Li,Na)NO<sub>3</sub>, (Na,Cs)NO<sub>3</sub>, each at two different compositions at a given temperature, and also pure LiNO<sub>3</sub> and pure KNO<sub>3</sub>, have been performed with the aim of reproducing the Chemla effect. The internal mobilities have been calculated directly by a Green-Kubo relation between mobility and the time integral of collective velocity correlation functions.<sup>1</sup>

In previous MD investigations of the Chemla effect in alkali halides mixtures,<sup>1</sup> non-polarizable pair-wise additive potentials have been used, in which the model parameters are different at each composition of a given system. The role played by anion polarization on the Chemla effect in molten alkali nitrates is demonstrated here by comparing the calculated internal mobilities using non-polarizable and polarizable models. Polarization effects were included in the simulations by using a previously proposed fluctuating charge model (FCM) for the glass-forming liquid 2Ca(NO<sub>3</sub>)<sub>2</sub>.3KNO<sub>3</sub> (CKN).<sup>2</sup> It is shown here that a *single* potential model for a given (M<sub>1</sub>,M<sub>2</sub>)NO<sub>3</sub> system results in the correct composition dependence of the M<sub>1</sub> and the M<sub>2</sub> internal mobilities provided that polarization effects are included in the model. The FCM for the nitrate anion is thus transferable between different systems, but not its non-polarizable counterpart.

*Acknowledgments.* The author is indebted to FAPESP and CNPq for financial support.

1. See the recent review: I. Okada, *J. Mol. Liq.* **83**, 5 (1999).
2. M. C. C. Ribeiro, *Phys. Rev. B* **61**, 3297 (2000); **63**, 094205 (2001).

## DEPENDENCE OF THERMAL CONDUCTIVITY IN MOLTEN SALTS ON IONIC MASS

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Accurate determination of thermal conductivity is extremely difficult for molten salts at high temperature since many errors are caused by thermal radiation, convection and intrinsic properties of molten salts such as corrosiveness and ionic conductivity. Molecular dynamics (MD) simulation is useful for the evaluation of thermal conductivity of molten salts since it is free from such experimental difficulties. Moreover, it enables us to investigate the dependence of thermal conductivity on each thermodynamic variable such as temperature and density. So far, we have evaluated the thermal conductivity of a series of molten alkali halides using MD simulation and the Green-Kubo technique. The obtained results are in quantitative agreement with experimental ones. In addition, it was found that the calculated thermal conductivity depends not on temperature but number density[1].

In the present study, we investigated the mass dependence for some molten LiI and CsF. It is a great advantage of MD method that ionic mass can be easily changed as an independent variable for the evaluation of physical properties. The calculated thermal conductivity decreased with increasing ionic mass in both molten salts. The change of ionic mass is expected to influence the phonon frequency. Hence, the phonon velocity of longitudinal optic mode was evaluated from charge-charge dynamic structure factors for LiI and CsF as a function of ionic mass. The calculated phonon velocity increased with decreasing ionic mass for both molten salts. On the other hand, the relationship was discussed between the thermal conductivity and the experimentally obtained sound velocity for a series of molten alkali chlorides. For these systems with different ionic mass, no change in liquid structure was observed for the radial distribution functions. It has, therefore, been concluded that the thermal conductivity is directly affected by ionic mass and is directly proportional to the phonon velocity in the same way as insulating solids.

[1] K. Takase, T. Oono, I. Akiyama and N. Ohtori, EUCHEM Conference on Molten Salts, 2000.

## Structure of molten $\text{PbF}_2$ obtained by EXAFS spectroscopy

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EXAFS spectroscopy has been recently exploited for elucidating the structure of several molten salts with complementary use of X-ray and neutron diffraction techniques. We have measured the EXAFS spectra of  $\text{PbF}_2$  and  $\text{PbF}_2\text{-LiF}(x_{\text{Pb}}=0.6)$  at various temperatures in order to obtain deep insight information of these melts as one of the candidates of blanket material for fusion reactor in future. It is well known that the orthorhombic crystal structure of  $\text{PbF}_2$  at room temperature transforms at ca. 589 K into the cubic structure. Additionally,  $\text{PbF}_2$  in solid phase at more than 711 K (this temperature is less than its melting point, 1128 K) shows superionic conductance. The purpose of this study is also to find how these transforms reflect to EXAFS spectra.

The temperature dependence on extracted vibration  $\chi(k)$  from EXAFS spectra by using Pb LIII edges show clearly phase shift between 676 K and 777 K, concerning not with crystal phase transformation but with superionic conductance transformation, as we have not expected. More striking behaviour occurs if we elevate the sample temperature until less than its melting point. These spectra show clear phase shift again between 675 K and 795 K, however, we obtain almost the similar spectra with these on higher solid phase after cooling. The structural function obtained by Fourier transformation of EXAFS spectra show there are not so much difference between the structure of solid at higher temperature and the melt. For fair evaluation of these structural results obtained by EXAFS, molecular dynamics simulation of molten  $\text{PbF}_2$  is required and now progressing.

## VISUALIZATION OF MD RESULTS ON CRYSTALLISATION OF MgO FROM ITS MELT

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We have previously studied crystal growth from supercooled NaCl, MgO and CaCl<sub>2</sub> melts by molecular dynamics (MD) simulation. For MgO, we have already reported the main results.<sup>1)</sup> In the present study, for more explicit presentation of its crystal growth, the motion of the ions has been visualized. As the software for the visualization the Pov-Ray was used.

The MD model is schematically shown in Fig. 1. The periodical boundary condition was imposed in the x-, y-directions, but not in the z-direction which was open to a vacuum. At first 1400 ions were disposed in the perfect crystalline state (NaCl-type) in 14 layers and the upper 10 layers were heated sufficiently higher than the melting point, and thereby liquid phase was generated on the 4 crystalline layers. The melting point was estimated from conventional 3-dimensional MD to be 2670 K, while the (experimental) melting point is 3099 K. The two-dimensional Ewald method was used for calculation of the coulombic force.

The crystal growth from the melts has been studied on the (100), (110) and (111) planes. The ions at the 1<sup>st</sup> (bottom) layer were kept unmoved during the whole runs so that the system was stable with respect to the basic cell frame. In the case of the (111) system, 50 Mg<sup>2+</sup> instead of 100 Mg<sup>2+</sup> were arranged on the first layer and on the 5<sup>th</sup> layer; because, if 100 Mg<sup>2+</sup> were placed on the 1<sup>st</sup> layer, the system was unstable due to the repulsion. Further, in the (111) system the 100 O<sup>2-</sup> ions on the 2nd layer were also held unmoved.

The results of the constant length (along x- and y-directions) run at 2500 K have been visualized, while MD simulation has been done at various conditions of temperatures and pressures. The motions of the ions are viewed from the z-direction as well as from the y-direction. In the former case, the picture of each layer is viewed. The ionic radii of Mg<sup>2+</sup>(VI) and O<sup>2-</sup>(VI) are 72 pm and 140 pm, respectively. The ionic radii on the picture are reduced by a factor of ca. 2 for a clearer view.

In the (100) system the crystal grew by 10 layers in ca. 50 ps, although some ions were left on the 15<sup>th</sup> layer the number of which corresponds to that of the defects in the crystal. Also in the (110) and (111) systems, crystal seemed to grow locally in the <100> direction. Thus, crystal

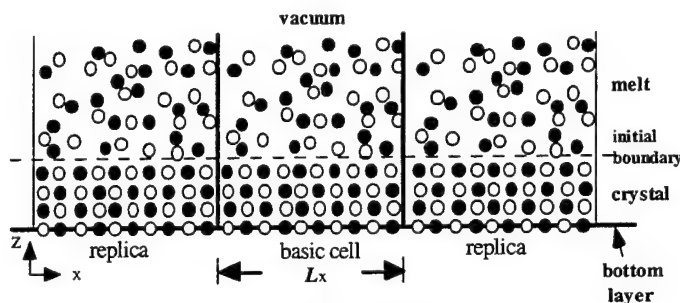


Fig. 1. Model cell for crystallization.

preferably grows in the <100> direction in MgO, which is the case also with NaCl.

<sup>1)</sup> I. Okada, Y. Utsunomiya, H. Uchida and M. Aizawa, *J. Mol. Liq.* **2002**, 98-99, 191-200.

**The application of the new model of electric double layer  
of electrodes in molten salts in the study of electrode reactions  
in magnesium and aluminium electrolysis**

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As pointed out by Parsons [1] there is no general model of electric double layer of electrodes in molten salts. A new model of electric double layer of electrodes with and without faradaic current in molten salts has been developed [2]. Similarly to other solvents, the double layer is assumed to be composed of two layers: the Helmholtz compact layer and the diffuse layer. The Helmholtz compact layer consists of the primary solvation shell, composed of adsorbed anions and/or neutral molecules.

For electrodes with faradaic current the charge density of the compact Helmholtz layer is calculated from the charge of the closely packed anions, decreased by the charge neutralised by the faradaic and/or outer current flowing through the interface and the adsorption of neutral molecules. For ideally polarisable electrodes (no faradaic current) the capacitance of the compact layer is the Helmholtz capacitance. The diffuse layer which extends from the end of the compact layer  $x_0 = 2r_{Cl^-}$ , is formed by the counterions to the ions adsorbed specifically in the primary solvation shell. These counterions (for alkali halide melts the counterions are the alkali cations) are distributed in the numerous holes, which are introduced into the molten salt structure by the melting process.

The anode reactions in the aluminium and magnesium electrolysis are complicated by the adsorption both of some neutral species and/or intermediate compounds, which also decrease the charge of the primary solvation shell. It will be shown that from the evaluation of the experimental double layer capacitance the coverage of the anode may be obtained.

## References

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2. A. Kiswa, *J. Electroanal. Chem.* In press.

## APPLICATIONS OF MOLTEN SALTS FOR PRODUCTION OF REFRACTORY METALS

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In Russia, zirconium is produced on an industrial scale by the electrolysis of chloride-fluoride melts containing  $K_2ZrF_6$ . The main harmful impurity in zirconium being hafnium. The possibility to decrease its concentration in metallic zirconium during electrorefining from chloride-fluoride melts has been studied.

Tests on the production of niobium powder were performed in an industrial electrolyzer for production of zirconium. The process was carried out with current, 8-11 kA, initial cathodic current density,  $2.6-3.3 \text{ A cm}^{-2}$  and anodic current density,  $0.15-0.20 \text{ A cm}^{-2}$ . The pentachloride of niobium was used for feeding the electrolytic bath. Optimal parameters of electrolysis, such as niobium concentration, initial cathodic current density and temperature have been determined. The influence of the process parameters on the purity of niobium powder and its grain-size has also been investigated.

The method of galvanoplastics was used for production of hafnium cathodes for powerful electronic lamps.

Articles based on graphite are widely used in high-tech field because of the unique properties of graphite. However, a drawback of graphite-based composites is their low heat resistance in an oxidizing atmosphere. To increase the heat resistance of graphite articles siliconizing and borosiliconizing are currently used. However, articles of borosiliconated graphite are operable a limited period of time and at temperatures up to  $1200^\circ\text{C}$  only. In order to prevent graphite oxidation for a temperatures up to exceeding  $1500-1700^\circ\text{C}$  protective coatings of hafnium and hafnium-niobium alloy with a mixed ( $\alpha+\beta$ )-structure obtained by molten salt electrolysis gave coherent and poreless coatings of desired compositions. A thin layer of hafnium carbide formed at the first electrolysis stage does not influence the physico-chemical and mechanical characteristics of the composite due to its small thickness ( $<1 \mu\text{m}$ ), but prevents interaction of hafnium and hafnium-niobium alloys with the graphite. Composites with a graphite matrix and protective coatings of hafnium and hafnium-niobium alloys can be used for making units and mechanisms requiring operation for some time, in an oxidizing atmosphere, and at superhigh temperatures.

Laminated metallic copper-hafnium compositions were used as high-temperature solders for diffusional soldering of refractory metals.

Using disproportionation reactions in molten salts, the barrier layers from titanium and niobium were produced on glass-ceramic shells for hot isostatic pressing (HIP). The quality of articles from titanium alloys obtained by HIP in these shells has been studied.

## INERT ANODES FOR ALUMINIUM ELECTROLYSIS; A NEW TECHNOLOGY?

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The "hottest subject" in aluminium-related research is presently the development of inert anodes. In the existing Hall-Heroult technology for aluminium production a consumable carbon anode is used, producing CO<sub>2</sub> and intermittently also the powerful greenhouse gases CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. If inert anodes are introduced, the only anode product will be oxygen, according to the cell reaction,



and it will be an environmentally friendlier and more efficient process. The molten salt electrolyte (Na<sub>3</sub>AlF<sub>6</sub> - AlF<sub>3</sub> - CaF<sub>2</sub> - Al<sub>2</sub>O<sub>3</sub>) can either be the same or it can be modified to a more low-melting composition.

Research on inert anodes has been an active field for many years, with many groups involved. Still, it sent shock-waves through the aluminium industry and the research community when the world's largest aluminium company, Alcoa, in April 2000 announced that they were close to a technological breakthrough for the use of inert anodes. At present, Alcoa has a full-scale cell running with inert anodes, and an entire cell-room is scheduled to be in operation later this year. In view of this sensational development, we shall examine the inert anode technology, its strengths and weaknesses and present some relevant experimental results.

The inert anode material can be a ceramic, a cermet or a metal. In any case the working surface has to be an electronically conducting oxide. We shall have a close look at the Alcoa cermet anode, having nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) as its main component, with about 20% metal phase, being a Cu-Ni-Ag alloy. Cermets are attractive because they combine the chemical stability of the ceramic with the good electrical conductivity of the metal phase in the interior. The shortcomings of ceramics and cermets are problems producing large shapes, the brittleness of the materials and problems achieving stable electrical contacts.

With metal anodes all these problems are eliminated. However, metals are inherently unstable in an oxygen atmosphere at high temperatures (850 – 950 °C), so the metal must be covered by a dense, coherent oxide layer at all times. Compositions being tested are mainly Cu-Ni-Fe and Fe-Ni alloys. Low-melting electrolytes (high excess AlF<sub>3</sub> contents) are preferred in order to reduce the rate of oxidation of the metal phase.

Some data will be given to illustrate the problems caused by the fact that all oxide materials have a finite solubility in the electrolyte, leading to wear of the anodes and contamination of the aluminium, when the dissolved species are being reduced at the cathode. Although the wear of the anode material caused by slow dissolution (1 – 2 cm/year), can be tolerated, the accompanying contamination of the metal produced is perhaps the most serious problem facing inert anode research and development.



## TREATMENT OF MOLTEN SALTS WASTES BY PHOSPHATE PRECIPITATION

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Pyrochemical reprocessing of spent nuclear fuels using high-temperature molten salts is one possible alternative for existing extraction technology. Melts based on the eutectic mixtures of alkali metal chlorides are amongst the favoured candidates. After the spent fuel is dissolved in the melt, and uranium, plutonium and heavier actinides are removed, the melt needs to be cleansed from the remaining fission products and corrosion products, before it can be reused.

Precipitation of the fission products as phosphates may offer an acceptable solution. Most of the inorganic phosphates are insoluble in chloride melts and thus these precipitates can easily be separated from liquid melts. Separating wastes in phosphate form is also particularly convenient for subsequent vitrification, since phosphates form very stable non-leachable glasses that moreover are very stable in a highly radioactive environment.

In the present work we have studied the reactions of alkali metal phosphates with chloride melts containing the elements found during reprocessing of spent nuclear fuels. These include Cs, Mg, Sr, Ba, lanthanides, Zr, Cr, Mo, Mn, Re (to simulate Tc), Fe, Ru, Ni, Cd, Bi and Te. The experiments were conducted in LiCl-KCl-based melts at 550 °C and in NaCl-KCl-based melts at 750 °C using lithium and sodium orthophosphates, respectively, as precipitants. A range of phases insoluble in the melts was formed. The products precipitated included normal and double phosphates, oxides and metals. The distribution of the elements between molten salts and solid precipitates was determined. Reactions in melts containing two or three elements (chosen from Sr, Ba, Ce and Zr) were also investigated.

Caesium could not be removed from the melts by this technique. A preliminary study was therefore conducted using double phosphates as possible ion exchange materials for removing Cs from chloride melts. The compounds tested were  $\text{Na}_3\text{Ln}(\text{PO}_4)_2$  (Ln = La, Ce, Pr, Nd, Gd and Dy) and  $\text{KZr}_2(\text{PO}_4)_3$ . The distribution of caesium between the melt and the solid phase was followed radiometrically using  $^{137}\text{Cs}$ . The experiments were conducted in LiCl-KCl and NaCl-KCl-based melts in the range 450 to 750 °C. The effects on the ion-exchange process of time, temperature and composition of the solid phase were investigated. The effect of *in situ* preparation of double sodium-lanthanide phosphates on caesium uptake into phosphate was also studied. Although the materials investigated were not efficient for caesium removal the experiments allowed evaluation of trends in the sorption behaviour of this element in chloride melts.



# Carbon Electrodeposition Process in Molten Fluorides

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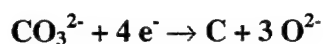
<sup>2</sup> *CEA/VALRHO, DEN/DTE/STME, BP 111, 26702 Pierrelatte Cedex, France*

## Abstract

Carbon is currently used as anode material in several electrochemical processes, either in pure form or alloyed with other elements, due to its properties such as high heat resistance, corrosion resistance in oxidizing conditions and low cost. So, a coating of carbon on usual conductive metals such as copper should yield a material with attractive properties for use as an anode in electrochemical processes; this new type of anode should offer both the properties of the substrate (mechanical resistance and electrical conductivity) and the surface properties of carbon (corrosion resistance and electrocatalytic properties).

The first part of this work presents a study of the electrochemical reduction mechanism of carbonate ions  $\text{CO}_3^{2-}$  into carbon in  $\text{LiF-NaF-Na}_2\text{CO}_3$  media in the 700-800°C temperature range, by using cyclic voltammetry and chronopotentiometry.

The cathodic peak in the cyclic voltammogram indicates that  $\text{CO}_3^{2-}$  ions are reduced in a one-step process:



Moreover, in this work the possibility of using carbon dioxide  $\text{CO}_2$  as a source of carbonate ions in a bath containing oxide ions  $\text{O}^{2-}$  was examined. Finally, deposits of amorphous carbon were obtained by potentiostatic electrolysis and analysed by several physical techniques: X-ray diffraction, Raman spectroscopy, scanning electron microscopy coupled with energy dispersive spectroscopy.

Then, in a second part, the electrochemical nucleation of carbon in molten alkaline fluoride media was investigated using cyclic voltammetry, chronopotentiometry and chronoamperometry in the 670-750°C temperature range. Chronoamperometric results show that the deposition process involves progressive nucleation with diffusion-controlled growth of the nuclei, and scanning electron microscopy shows that the shape of the nuclei is hemispherical.

## VISCOSITY OF MOLTEN RARE EARTH CHLORIDES

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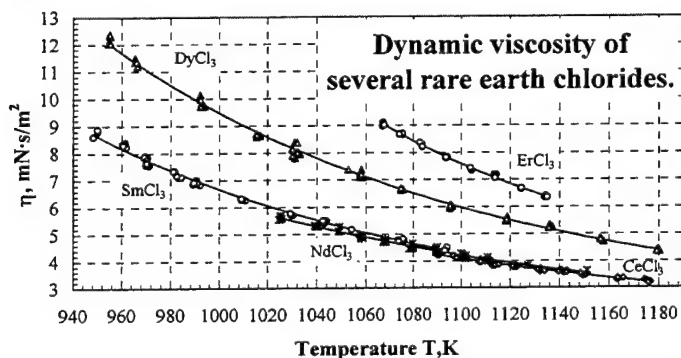
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At the present time salts of rare earth metals are widely used in many areas. At the same time viscosity of these salts in molten state is studied insufficiently. Some odd data available are doubtful itself and are in contrary to each other. There are two main reasons of these discrepancies. The first is inadequate dehydration, when oxychloride impurities distort the results. The second is not enough inert atmosphere during handling or measurements, which also leads to formation of oxychlorides at the high temperature. Products of interaction with water can influence on the measured viscosity itself and can change it due to corrosion attack on the container material.

In this study, kinematic viscosity ( $\nu$ ) of five molten rare earth trichlorides ( $\text{CeCl}_3$ ,  $\text{NdCl}_3$ ,  $\text{SmCl}_3$ ,  $\text{DyCl}_3$  and  $\text{ErCl}_3$ ) was measured by using a capillary viscometer made of quartz. Special attention was paid on careful dehydration of the salts under investigation. Initial chlorides were dried in the  $\text{N}_2$  and  $\text{HCl}$  flows under gradual heating within several days. After melting the salts were filtered by means of the quartz filter. Distillation under reduced pressure ( $\sim 1\text{Pa}$ ) was the final preparing stage. All handling operations were performed in dry box with water content less than 1 ppm. The capillary viscometer was constructed as completely sealed quartz vessel and thus any contact with moisture was excluded. Only under such conditions it becomes possible to obtain the viscosity data being in close agreement.

The dynamic viscosity was computed by the expression  $\eta = \nu \cdot d$  where  $d$  – density [1]. The results obtained are shown in Fig. The viscosities of  $\text{CeCl}_3$ ,  $\text{NdCl}_3$  and  $\text{SmCl}_3$  are very close



to each others. For example, they coincide within 1.6% at 1100 K. The viscosities of  $\text{DyCl}_3$  and  $\text{ErCl}_3$  are essentially higher. The viscosity of molten  $\text{CeCl}_3$  and  $\text{ErCl}_3$  was measured for the first time. No literature data were found. The viscosity of fused rare earth chlorides increases as temperature decreases as well as on going from cerium trichloride to erbium

trichloride. By now it is well proved that molten individual rare earth chlorides form a loose network like structure. The melts with the small cation size form a more rigid net-work with presumably long " $\text{LnCl}_6$ " octahedra life times [2]. Our results are in excellent agreement with this structure data. Due to every lanthanide cation has six  $\text{Ln}^{3+}\text{-Cl}^-$  links absolute viscosity of such melts relatively high (for example at 1073 K 1.0 for  $\text{NaCl}$  against 6.7  $\text{mN}\cdot\text{s}/\text{m}^2$  for  $\text{DyCl}_3$ ) and increases as network becomes more rigid from Ce to Er.

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## Morphology and Formation Mechanism of Electrodeoxidized Niobium Metal in Molten Chlorides

X. Y. Yan and D. J. Fray\*

### ABSTRACT

Niobium powder and sponge have been produced from pellets of  $\text{Nb}_2\text{O}_5$  in a  $\text{CaCl}_2$ - $\text{NaCl}$  eutectic melt at temperatures between 850 and 950 °C by electrodeoxidation. The cathode products after electrolysis were characterized by the techniques of the scanning electron microscopy (SEM) with an energy dispersive X-ray analysis (EDXA) and the X-ray diffraction (XRD). The samples were also analyzed for the oxygen content. The results obtained were consistent with the thermodynamic analysis of the Nb-Ca-Cl-O system over the temperature range studied. The morphological features in the final cathode products were found to be (1) equiaxed metallic particles contacted loosely and these could be ground manually into the micro-sized niobium powder; (2) equiaxed metallic particles contacted firmly, forming an interconnected porous network in the niobium matrix; and (3) niobium sponges had a structure similar to that of the Kroll titanium sponge. The relationship between the processing parameters and the morphology of the products was investigated. Finally, the formation mechanism of electrodeoxidized niobium metal from the  $\text{Nb}_2\text{O}_5$  pellets in the chloride melts was proposed based upon the present experimental observations.

For correspondence, please contact Professor D J Fray\*

## Scaling relationships for freezing points of liquid ionic salts

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Since the neoteric ionic liquids were discovered at USAFC in the early 1980's [1], the reason for their existence at low temperatures has been clouded. Unlike most other classes of atomic or molecular liquids, the characteristic energy of ionic liquids decreases with the characteristic distance. Ionic liquid freezing temperatures, roughly vary inversely with unlike interionic distance. Recent experimental studies [2] confirm this correlation with density for the room temperature ionic liquids.

Ionic crystal melting points, in general, are readily explained from scaling considerations [3]. In the primitive ionic system the dominant free energy difference between crystal and liquid phases is electrostatic. In a one-distance parameter model the melting point of a 1-1 ionic crystal is  $T_m = 0.0165e^2/k_B (\sigma_+ + \sigma_-)$  where  $e$  is the electron charge,  $k_B$  is Boltzmann's constant and  $\sigma$  is the ionic radius. For highly asymmetric salts, first order perturbations, moreover, of like-ion overlap interactions, or polarization, show that these complications lower the reduced melting points even further.

This reduced melting point of cubic ionic crystals are 50-100 times lower than the counterpart reduced melting points of other classes of crystals, such as atomic, molecular, polar or metallic. The reason for this lies in the short-range packing symmetry. We have begun to explain the peculiar phase diagrams of a number of binary systems, including also binary metal alloys, starting from the scaling of non-additive spheres [4]

Simulations on non-additive mixtures of binary spheres have been undertaken. For rigid spheres a nonadditivity parameter ( $\alpha$ ) defines the like and unlike pair potentials

$$\sigma_{ij} = \alpha_{ij}(\sigma_i + \sigma_j)/2 \quad \text{and} \quad \alpha_{ij} = 1 + \delta_{ij}(\alpha - 1)$$

(using the kronecker  $\delta_{ij}$ ). With the above definition, like ions interact with a larger diameter. Computations have also been performed on non-additive soft (m-n) ionic reference systems (referred to as WCA after the reference system cut-off at  $\sigma_{ij}$  for the perturbation theory of simple liquids). Melting points of these systems have been computed.

When the results for non-additive spheres are scaled onto WCA-ionics, the larger value of  $\alpha$  corresponds to a smaller ion size. Thus, a crystalline system of larger ions is less stable with respect to the fluid phase than a system of smaller ions. Similar considerations for smaller values of  $\alpha$  affect the stability of the body-centred CsCl-structure salts. These preliminary results help to further explain in a simple way the earlier corresponding observations for the alkali halides [3], and the low freezing points of ionic liquids.

## IONIC LIQUID CRYSTALS: FROM DISCOVERY UP TO PRESENT DAY

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Ionic liquid crystals (ILC) can be determined as thermodynamically equilibrium liquids that consist of unlike charged ions and possess a constant anisotropy of some physical properties, for example a birefringence. The ILC structure is stabilised by electrostatic forces acting between the ions, rather than through a large molecular length to width ratio normally considered essential for the existence of molecular liquid crystals.

A.R.Ubbelohde was the first to discover liquid crystals in ionic melts with organic ions and it was more than thirty years ago. Main trends of progress in the area of salt melts with liquid crystalline ordering have been discussed in this report.

The extensive and systematic studies of structure, thermodynamic and transport properties and mesomorphic behaviour of the pure salts and their binary mixture with both the common anion and cation have been carried out. From these results the main regularities and criteria of thermotropic ILC formation and stability in the salt systems with organic anions have been established. Among them is the relationship between the capability of organic salt to form ILC and its cationic and anionic parameters (ionic size and charge). Moreover, an important role of crystal structure responsible for the mesogenic behaviour of ionic compound has been found. At last, a character of interionic interactions in binary systems has been shown to be a factor, which may regulate the temperature-concentration range of ILC existence.

It is shown that ILC present a new class of ordered ionic solvents which combine the properties of usual ionic liquids with ones of liquid crystalline solvents. They may be promising materials for their application as universal solvents for modern fields of techniques such as optoelectronics and laser techniques.

## POLYMERIZABLE IONIC LIQUIDS AND THEIR POLYMERS FOR ION CONDUCTIVE FLEXIBLE MATRIX

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Advanced polymer systems having unique characteristics of ionic liquid are prepared by the polymerization of a series of polymerizable ionic liquids. Since alkylimidazolium-type ionic liquids show excellent physico-chemical properties, their vinyl derivatives have been synthesized. They are obtained as liquid with very high ionic conductivity when suitable anion was selected, but the ionic conductivity was considerably lowered after polymerization<sup>1</sup>. This was attributed to be due to the decrease of molecular motion. Introduction of spacer group between vinyl group and imidazolium cation greatly improved the ionic conductivity after polymerization. Furthermore, polyanions having free alkylimidazolium cations showed much higher ionic conductivity than imidazolium cation-based polycations with corresponding counter anions.

Other types of polymerized ionic liquid will also be mentioned. For examples, both cations and anions were fixed on the polymer chains to inhibit the migration of component ions. This zwitterionic salt was obtained as liquid when this was mixed with lithium bis(trifluoromethanesulfonyl)imide. This mixture was further mixed with polar polymer matrix as non-volatile polymer gel electrolytes. Polymerizable zwitterionic salt was synthesized and polymerized<sup>2</sup>. Copolymerization of vinylimidazolium vinylsulfonate was also examined to prepared polymeric domains where no mobile ions were existed<sup>3</sup>. These polymers should be used as polymer solvent for electrochemical applications by adding suitable (target) salt.

Some future applications with these polymerized ionic liquids will also be mentioned.

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- 3) M. Yoshizawa, W. Ogihara, and H. Ohno, *Polym. Advanced Technol.*, 2002, in press.

## GROUP 15 BASED QUATERNARY SALTS: THE DEVELOPMENT OF IONIC LIQUIDS WITH LARGE ELECTROCHEMICAL WINDOWS.

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We are studying ionic liquids as solvent media for the electrochemical deposition of electropositive metals. Our current goal is to prepare new air stable ionic liquids with large electrochemical windows to allow the deposition of actinides of relevance to nuclear fuel processing.

We have recently investigated the effect of chemical composition on the electrochemical properties of novel air-stable low-melting quaternary triflates and triflimides. A range of new quaternary salts have been synthesised to study the effect of the nature of central atom and organic substituent on physical, electrochemical and thermal properties of these compounds. The prepared salts were characterised using various spectroscopic techniques and single crystal X-ray crystallography. The group trends were assessed using tetramethyl and triphenylmethyl salts, and the effect of aryl and alkyl groups on the cation have also been investigated with the aim of decreasing the melting point.

The electrochemical measurements were performed in pure molten salts and solutions in acetonitrile using internal reference agents. An electrochemical window of up to 6.5 V stability was measured using glassy carbon electrodes. It was possible to observe the electroreduction of Sm to Sm(0) in some of the prepared ionic liquids, one of the most electropositive of the *f*-elements. In theory it should be possible to electrodeposit uranium and plutonium in many of these novel ionic liquids.

## MICROSTRUCTURE AND CRYSTALLISATION HISTORY OF MOLTEN SALTS DECODING BY MEANS OF THE HOMOGENEOUS REGIONS BORDERS MODELS

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Difficulties of the experimental investigation of multicomponent ( $n \geq 4$ ) phase diagrams (PD) and efforts, consisted with the necessity to co-ordinate and to estimate the reliability of experimental results, require to combine both the experimental and the thermodynamic simulation. The more components form a system the more complicate thermodynamic model has to be used. And although such powerful programs as for instance THERMOCALC are able formally to calculate systems formed by any number of components, their application is blocked by the absence of experimentally determined thermodynamic parameters. In such a case the required for the model construction insufficient data is substituted for a "theoretical" significance. As a result we get for a real system some diluted and maximal formalising model. And it is even possible that some elements of such model have no physical sense. If the multicomponent system description formalisation is inevitable then such direction of the computer-aided design (CAD) of materials as the heterogeneous design becomes the very perspective one. It is based on the fact that ruled hypersurfaces predominate among geometrical elements of the PD. The mathematical description of ruled elements does not require additional thermodynamic parameters. All experimental information are concentrated in the equations of unruled hypersurfaces. The last are boundaries of one-phase regions (liquidus, solidus, solvus). The adequacy of these equations to experimental results reflects the reliability and the quality of the experiment. Further verification of experimental data will correct these equations of homogeneous regions only and will not influence on another description of the PD. The main rules of geometrical thermodynamics (the phase rule, the rule of bordered state spaces, the extension rule etc.) are consisted in the PD thermodynamic description and are fulfilled automatically. Whereas it is to foresee the observance of these rules by the "purely" mathematical model. However this defect is compensated by the simplicity and the convenience of the model. So as a result such mathematical model of the PD as a system of unruled hypersurfaces equations makes possible: 1) to determine phase regions borders and to calculate co-ordinates of nonvariant equilibrium points; 2) to research the PD construction by iso- and polythermal sections of various dimensions; 3) to calculate mass quota and concentrations of coexisting phases on all liquid crystallisation paths; 4) to simulate situations of priority participation in peritectic reactions more disperse crystals. Projections of boundaries of all phase regions, situated above a given phase region down to the temperature axis, divides the region into thermodynamically unstable fragments. Each fragment differs by the set of coexisting phases which passed through various crystallisation stages. Maximal distinction is reached by projecting of all PD hypersurfaces to the concentration simplex. The last is divides to fields. Each field has its own crystallisation scheme and hence its own unique microstructure. In the end to have the set of equations of unruled hypersurfaces (borders of one-phase regions) it means to solve straight and inverse tasks: to calculate the initial liquid concentration for the crystallisation according to the given scheme or on the contrary to find out all stages of the crystallisation from the given concentration liquid.

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## MOLTEN SALTS IN BATTERY MATERIALS

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Many battery materials are made by high temperature solid state syntheses. These have the advantage that the required products can be made but these syntheses are inevitably slow and energy intensive because of the high temperatures needed and the long time for the syntheses. Solid state syntheses can be carried out on the laboratory scale, e.g. 5 g, using simple furnaces but production in larger quantity usually needs high cost rotating furnaces to ensure even mixing of reactants and products. Solid state syntheses are limited by diffusion of ions through solid materials which is slow. Use of molten salts avoids these problems. Provided that at least one of the reagents is soluble in the molten salt, the temperature of reaction is limited to the melting point of the molten salt. Ideally both reactants should be soluble in the molten salt but successful reactions have been achieved when only one reagent is soluble. If necessary, eutectic mixtures can be used to reduce the melting point of the molten salt solvent. The reaction normally takes place instantly once the molten salt solvent has melted. Hence the reaction is much faster than solid state syntheses. Once the reaction has taken place, the reacted mixture can be cooled to room temperature. The molten salt solvent will need to be removed. This can often be done by dissolving it out with a solvent which dissolves the molten salt, but which does not react with the desired product. The molten salt and the solvent used to dissolve it from the product can be recycled, so molten salt syntheses can be environmentally friendly.

The use of molten salt syntheses for making battery materials will be described.

N.B. This talk will be based on the talk given at the Molten Salt Discussion Group of the Royal Society of Chemistry in December 2001

## **New functionalised ionic liquids and their commercial availability**

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### **Abstract**

Merck KGaA is a Germany based pharmaceutical and chemical company with a 333 year history, and has a broad experience in the supply of high quality solvents through VWR, a 100% owned subsidiary of the Merck company. Building on our experience concerning the manufacture of aluminium chloride based ionic liquids, and the production of high quality battery materials, we have progressed into the innovative area of developing and manufacturing a range of new ionic liquids solvents. This presentation addresses issues relevant to the commercial availability of new ionic liquids, with particular emphasis on halogen free ionic liquid and on alternatives to hexafluorophosphates and  $(\text{CF}_3\text{SO}_2)_2\text{N}^+$ . Among the topics to presented are: physical / chemical properties and environmental concerns.

## LOW TEMPERATURE MELTS FOR ELECTRODEPOSITION OF METALS

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Low temperature ionic melts (LTIM) based on stable organic compounds are prospected media for applications in chemical and electrochemical technologies. Aqueous solutions contained harmful components, for example cyanides can be substituted on the melts without of considerable change in technological scheme. The operating temperatures of aqueous solutions for majority electroplating, etching etc. processes are 30 – 60°C. There for, the melts with the m.p. below 40 – 50°C are quite suitable to carried out the processes mentioned above.

LTIM can be divided conventionally on two main series, namely protic and aprotic solvents. The first one studied melts unite carbamide, acetomide, imidazol systems. Ionic conductivity in the systems is created by NH<sub>4</sub>Cl addition, so that cathode process is limited of hydrogen evolution as well as in aqueous electrolytes. These LTIM are eligible for electrodeposition and separation of noble metals, copper etc. Etching and polishing processes in such systems can be applied for the treatment of refractory metals. Imidazole based melts have been used for electrodeposition and separation of silver and copper.

It can be picked out the systems based on 1-methyl-3-ethylimidazolium salts from the second group of the electrolytes, which are in the first place interested for the electrodeposition of refractory metals, aluminium etc. But, only single step corresponding to Ta<sup>5+</sup>/Ta<sup>4+</sup> and Nb<sup>5+</sup>/Nb<sup>4+</sup> transfers were recorded by previous investigations.

We have investigated electrochemical properties of LTIM based on quaternary ammonium salts, namely chlorides of tetrabutylammonium, triethylpropylammonium and diethylbicyclooctane.

Electrochemical behavior of AlCl<sub>3</sub> and TaCl<sub>5</sub> compounds in these systems is discussed in present report.

Aluminium coatings, dendrites and Ta-Al alloys were obtained using both soluble (Al, Ta) and insoluble (Pt) anodes.

## TEMPERATURE DEPENDANCE OF VISCOSITY AND CONDUCTIVITY FOR VARIOUS ROOM TEMPERATURE IONIC LIQUIDS

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We have designed and constructed a rolling ball viscometer to record the viscosity of room temperature ionic liquids outside the glove box. It has been calibrated with water and sucrose solutions (20, 40 and 60 %) at fourteen temperatures ( $10^{\circ}\text{C} \leq T \leq 70^{\circ}\text{C}$ ). The viscosity of ten air stable single salts and ten binary air sensitive chloroaluminate ionic liquids have been measured (at ten temperatures) and their activation energies for viscous flow calculated.

We have also designed a conductivity cell, which records conductivity as a function of temperature. Cooling and warming curves for the room temperature ionic liquids have been obtained (over a temperature range from  $25^{\circ}\text{C}$  down to  $-150^{\circ}\text{C}$ ).

# **POSTERS**

## POSTERS

- P1. **Mesomorphic Behavior and Optical Properties of Some Molten Divalent Metal Alkanoates**  
T A Mirnaya, L S Sudovtsova\*, G G Yaremchuk and S V Volkov *Ukrainian Academy of Sciences, Ukraine*
- P2. **Electrochemical synthesis of high pure tantalum oxide from molten salts**  
L A Yolshina\*, A V Glebov and V Ya Kudyakov *Urals Branch of Russian Academy of Sciences, Russia*
- P3. **Preparation and properties of glasses obtained by recycling of secondary lead from acid battery plants**  
M Constantinescu, I Nuta\*, M Malki, C Bessada, P Echegut, and E M Anghel *Université d'Orléans, France*
- P4. **Oxide Solubility and Structural Properties of  $\text{NdF}_3\text{-LiF-MgF}_2\text{-Nd}_2\text{O}_3$  Melts**  
E Stefanidaki\*, G M Photiadis, C Konotoyannis, A F Vik and T Ostvold *FORTH, Greece*
- P5. **The investigation of electrochemical production of Mg-Nd alloys from oxyfluoride media**  
A A Titov\* and V H Novitchkov *State Institute for Rare Metals (GIREDMET), Russia*
- P6. **Joint electroreduction of lanthanum, gadolinium and boron ions in chloride-fluoride melts**  
H B Kushhov, M K Vindizheva, A S Usdenova and Z A Zhanikaeva *Kabardino-Balkarian State University, Russia*
- P7. **ESR Study of Electron Localization and Dynamics in Metal-Molten Salt Solutions: Comparison of M-MX (M = alkali metal) and Re-ReX<sub>3</sub> Melts (Re = rare earth metal)**  
O Terakado, P Poh and W Freyland\* *Universität Karlsruhe, Germany*
- P8. **Kinetics and Mechanisms of the Magnesium Electrode Reaction in Molten  $\text{MgCl}_2\text{-LiCl}$  Binary Mixtures**  
J Kazmierczak, A Kiszka\* and R Tunold *University of Wroclaw, Poland*
- P9. **Studies on the Selective Transport of Organic Compounds using New Ionic Liquids as Supported Liquid Membranes**  
L C Branco\*, J G Crespo and C A M Afonso *Universidade Nova de Lisboa, Portugal*
- P10. **Molecular Dynamics Study of Ionic Melts**  
E A Gontcharenko\*, P F Zil'berman and V S Znamenskii *Kabardino-Balkar State University, Russia*
- P11. **Effect of the Ionic Composition on the Formation of the Electrochemical Active Species of Niobium in Fluoride Melts on the Base of Raman Spectroscopic Studies**  
O Babushkina\* and G Nauer *K plus Center of Competence in Applied Electrochemistry, Austria*

- P12. **A Spectroscopic Investigation into Technetium and Rhenium Speciation in Chloride Melts**  
V A Volkovich, I May\*, H Steele, J M Charnock and B Lewin *The University of Manchester, UK*
- P13. **Induced Mesophases in Binary Melts Based on Caesium Butanoate**  
T A Mirnaya\* and D V Bylina *Ukrainian Academy of Sciences, Ukraine*
- P14. **Electrodeposition of Rhenium on Monocrystalline Straight and Bent Rhenium Substrates from Molten Salts**  
N O Esina\*, L M Minchenko and A A Pankratov *Institute of High-Temperature, RAS, Russia*
- P15. **Development of electrochemical separation methods for Molten-Salt Reactor fuel processing**  
P Soucek\*, F Lisy, R Zvenskova and J Uhlir *Nuclear Research Institute Rez plc, Czech Republic*
- P16. **Study of Carbon Nucleation in Molten Fluorides**  
L Massot\*, P Chamelot, F Bouyer and P Taxil *CEA/VALRHO, DEN/DTE/STME, France*
- P17. **Neodymium electrodeposition process in molten fluoride media**  
C Hamel\*, P Chamelot, A Laplace, J Lacquement and P Taxil *Université Paul Sabatier, France*
- P18. **Neutron Diffraction Study of Ionic Aggregation in Lead Halide Melts**  
Y Iwadate\*, Y Seki, K Fukushima, M Misawa, T Fukunage, T Nakazawa and Y Okamoto *Chiba University, Japan*
- P19. **Use of room-temperature ionic liquids for nuclear waster reprocessing: preliminary studies**  
I Billard\*, C Gaillard, K Lützenkirchen, A Labet and G Moutiers *IReS, CNRS and University L. Pasteur, France*
- P20. **Spectroscopic investigation of the structural properties of the  $\text{LnI}_3\text{-Al}$  ( $\text{Ln}=\text{Dy, Ho}$  and  $\text{A}=\text{Cs, Na}$ ) binary systems**  
G D Zissi and A Chrissanthopoulos\* *ICE/HT – FORTH, Greece*
- P21. **Dependence of Thermal Conductivity in Molten Salts on Packing Fraction**  
N Ohtori\*, T Oono, Y Togawa, Y Suzuki and K Takase *Niigata University, Japan*
- P22. **Raman Study of Sodium and Iron Double Oxides at High Temperature**  
N Ohtori\* and F Ueno *Niigata University, Japan*
- P23. **Structural investigation of vanadium – sodium metaphosphate glasses, using solid-state NMR and Raman spectroscopy**  
A Chrissanthopoulos\*, C Pouchan, G N Papatheodorou, F Fayon and D Massiot *ICE/HT – FORTH, Greece*
- P24. **Electrode Process in  $(\text{KCl-KF})_{\text{eut.}}\text{-Gd}_2\text{O}_3\text{Halide Melt}$**   
I Elizarova I V Tananaev *Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Russia*

- P25. **Joint Electroreduction of Gadolinium and Boron**  
G Bukatova\* and S Kuznetsov *Kola Science Center, RAS, Russia*
- P26. **Intervallence Charge Transfer of Couples Eu(III)/Eu(II), Sm(III)/Sm(II) and Yb(III)/Yb(II) in an Equimolar Mixture of Molten NaCl-KCl**  
S A Kuznetsov\* and M Gaune-Escard *Institute of Chemistry Kola Science Centre RAS, Russia*
- P27. **Electrochemistry and Electrorefining of Chromium in Chloride and Chloride-Fluoride Melts**  
S A Kuznetsov\* *Institute of Chemistry Kola Science Centre RAS, Russia*
- P28. **Contribution of the Spectrophotometry to the High Temperature Molten Salt Chemistry**  
S Bourg\* and J Lacquement *CEA Valrho Marcoule, France*
- P29. **Some Preliminary Results on Modified Titanium Diboride Coatings Produced by Electrochemical Synthesis from Molten Salts**  
J Sytchev\*, T Gabor, H Kushkhov and G Kaptay *University of Miskolc, Hungary*
- P30. **NMR Study of Molten Fluoride in Presence of Graphite**  
A-L Rollet\*, C Bessada and A Rakhmatoulline *CNRS Orleans, France*
- P31. **Cluster Model Structure of Alkali Metal Chloride Melts**  
V Kremenetsky *Kola Science Centre RAS, Russia*
- P32. **Organic Salts of the Thiocyanate Anion**  
J Pringle\*, J Golding, D R MacFarlane and G Deacon *Monash University, Australia*
- P33. **Galvanostatic Phase Formation at the Electrode-Molten Salt Interface**  
V A Isaev\* and O V Grishenkova *Institute of High Temperature Electrochemistry, Russia*
- P34. **Molten Salt Thermal Storage for Gas Turbines**  
M Wendt\* and R Van Hattem *CSIRO Australia, Australia*
- P35. **The Electrochemical Reduction of Oxygen in Molten Alkali Chlorides: Theoretical Consideration**  
E V Nikolaeva, V A Khokhlov\* and V N Nekrasov *Institute of High-Temperature Electrochemistry, Russia*
- P36. **Ionic Conductivity of Molten  $\text{PCl}_5\text{-MCl}_n$  (M-Polyvalent Metal) Mixtures**  
A Salyulev and V Khokhlov\* *Institute of High-Temperature Electrochemistry, Russia*
- P37. **Structure of Lead Silicate Glasses in the System  $\text{Na}_2\text{O-PbO-SiO}_2$ :  $^{29}\text{Si}$ ,  $^{23}\text{Na}$  and  $^{207}\text{Pb}$  Solid State NMR Study**  
I Nuta\*, C Bessada, F Fayon, P Florian, D Massiot *CNRS-CRMHT, France*
- P38. **NMR Signature of Al Dissolution in  $\text{NaF-AlF}_3$  Melts**  
C Bessada\* and I Nuta *CNRS, France*



- P39. **A New Family of Room Temperature Molten Salts Based on the 1-Alkyl-2-Methyl Pyrrolinium Cation**  
J Sun\*, D R MacFarlane and M Forsyth *Monash University, Australia*
- P40. **Electrochemical Behaviour of Rare Earths in Molten Chlorides. Application of Electrochemical Techniques in Pyrochemical Processes**  
Y Castrillejo\*, R Bermejo, A M Martinez, E Barrado and P Diaz Arocas  
*Universidad de Valladolid, Spain*
- P41. **Solubilization of Rare Earth Oxides Present in a Simulated Nuclear Fuel in Molten Chlorides**  
R Bermejo\*, Y Castrillejo, M Vega, R Pardo and P Diaz Arocas *Universidad de Valladolid, Spain*
- P42. **Electrodeposition Studies of Magnesium in the Eutectic LiCl-KCl Mixture**  
A M Martinez\*, B Borresen, G M Haarberg, Y Castrillejo and R Tunold *NTNU, Norway*
- P43. **Advanced Ionic Liquids: Zwitterionic Liquids**  
M Yoshizawa\* and H Ohno *Tokyo University of Agriculture and Technology, Japan*
- P44. **New Data on the Ultrasonic Velocity in Crystalline Alkali Chloride Eutectics Close to the Melting Point**  
V Kokhlov\* and V Minchenko *Institute of High-Temperature Electrochemistry, Russia*
- P45. **Prediction of Physicochemical Properties of the Selected Fuel Salt Compositions**  
V Kokhlov\*, V Afonichkin, A Salyulev, V Ignatiev and K Grebenkine *Institute of High-Temperature Electrochemistry, Russia*
- P46. **Study of the Anodic Gases Composition during Nd<sub>2</sub>O<sub>3</sub>-MgO Electrolysis in Fluorides Media**  
V Soare\*, I Surcel, C Gurgu and A Rus *Institute for Nonferrous and Rare Metals, Romania*
- P47. **Solubility and Dissolution Kinetic of the Nd<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> in Molten Fluorides**  
V Soare\*, C Gurgu, I Surcel and M Burada *Institute for Nonferrous and Rare Metals Bucharest, Romania*
- P48. **Spectroscopic Investigation of Cobalt(II) Chloride Complexes in Acetamide – Ammonium Nitrate Melt**  
S B Gadzuric, I J Zsigrai and R M Nikolic *University of Novi Sad, Yugoslavia*
- P49. **New Approaches to Synthesis: Microwave-Mediated Chemistry using Ionic Liquids**  
N E Leadbeater and H M Torenus\* *King's College London, UK*
- P50. **Electrochemical Study of Rare Earths in Molten (Li,K)Cl Eutectic for Dry Reprocessing of Hydrogen Absorbing Alloys**  
H Matsuura\*, H Numata, R Fujita and H Akatsuka *Tokyo Institute of Technology, Japan*

- P51. **Direct Electrolytic Preparation of Chromium Powder**  
G Z Chen\*, E Gordo and D J Fray *Fuel Cells University Technology Centre, Cambridge, UK*
- P52. **Electrolytic Reduction of Solid Titanium Dioxide to Titanium Metal in Molten Calcium Chloride**  
G Z Chen\*, E Gordo and D J Fray *Fuel Cells University Technology Centre, Cambridge, UK*
- P53. **Microstructure Design in the Systems Na/F, Cl, CO<sub>3</sub>, R (R=MoO<sub>4</sub>, WO<sub>3</sub>)**  
V P Vorob'eva and O G Sumkina *Buryat Scientific Center, RAS, Russia*
- P54. **Synthesis of Complex Titanium and Zirconium Oxide Nano-powders in Molten Nitrates**  
S V Volkov\*, S M Malyovanyi, E V Panov and A P Monko *V I Vernadskyi Institute of General and Inorganic Chemistry, Ukraine*
- P55. **Ionic Interactions of Actinide Halides**  
A Karaman and Z Akdeniz\* *University of Istanbul, Turkey*
- P56. **Structure of Rare-Earth/Aluminium Halide Complexes**  
Z C Onem and Z Akdeniz\* *University of Istanbul, Turkey*
- P57. **Application of Oxidimetry for Determining Speciation of VB-Group Metals in Molten Chlorides**  
B D Vasin, S V Maslov, V A Volkovich\*, A S Muhamedeev, I P Polovov\* *University of Manchester, UK*
- P58. **Joint Electrodeposition of Molybdenum and Tungsten and Products Molybdenum-Tungsten Alloys, Double Carbides from Oxihalide Melts**  
H B Kushchov, L M Beroeva and R A Karashaeva *Kabardino-Balkarian State University, Russia*
- P59. **I Determination of the Liquids in a Computer Simulation of the Li/KCl Mixture, and a Study of the Ionic Structure at the Solid/Liquid Interface**  
O Lanning\* and P A Madden *Oxford University, UK*
- P60. **Chemla Effect in Li/KCl: A Computer Simulation Study**  
B Morgan\* and P A Madden *Oxford University, UK*
- P61. **Raman Spectra of Ionic Liquids: Interpretation via Computer Simulation**  
P A Madden\*, M Wilson and F Hutchinson *Oxford University, UK*
- P62. **New Solvent Systems Based on Eutectic Mixtures of Quaternary Ammonium Salts and Hydrogen Bond Donors**  
A P Abbott, G Capper\*, D L Davies, R K Rasheed and V Tambyrajah *University of Leicester, UK*
- P63. **Phosphorus Species in Cryolite-based Melts**  
E W Thisted\*, G M Haarberg and J Thonstad *Norwegian University of Science and Technology, Norway*

- P64. **Cation Composition of a Solvent as a Highly Effective Tool for Control over the Chemical and Phase Composition of the Products of Electrochemical Synthesis of Refractory Metals Compounds in Molten Salts**

V V Grinevitch\*, A V Arakcheeva, V F Shamray and S A Kuznetsov *Baikov Institute of Metallurgy and Materials Science, Russia*

## MESOMORPHIC BEHAVIOR AND OPTICAL PROPERTIES OF SOME MOLTEN DIVALENT METAL ALKANOATES

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Molten divalent metal alkanoates are the representatives of so called ionic liquid crystals or ionic mesogens [1]. They are perspective compounds in developing the new liquid crystalline materials for recording and imaging information.

This work is devoted to research of phase behavior, mesomorphic and optical properties of the pure divalent metal alkanoates and the binary systems based on them.

Phase transformations of homologous series of Mg, Ca, Sr, Ba, Zn, Cd, and Pb alkanoates have been studied by differential thermal analysis, polarization microscopy and small angle X-ray scattering. Among this group of salts lead and cadmium decanoates are shown to have a special interest as the components of binary mesomorphic mixtures due to their mesogenicity and low melting temperatures. Phase diagrams of binary liquid crystalline systems from metal decanoates with isovalent (Pb-Cd, Pb-Zn, Cd-Zn, Pb-Sr, Cd-Sr) and heterovalent (Pb-Li, Pb-Na, Pb-Tl, Cd-Na, Cd-K, Cd-Tl) replacement of lead or cadmium cations have been investigated.

It is found the continuous liquid crystalline solutions have been formed in the systems with both enantiotropic mesomorphic components. The intermediate liquid crystalline solutions have been formed in the systems where one component possesses monotropic mesomorphism (such as Cd decanoate) and the limit liquid crystalline solution have been formed in the systems where one component is nonmesogenic (such as Li or Zn decanoates).

Liquid crystalline solutions have been used as matrices for investigations of electronic absorption spectra of the 3d transition metals ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ) incorporated into the matrices as dopants. These studies have been carried out to explore the solvent properties of molten metal decanoates and coordination state of 3d transition metals in these media.

On the basis of comparison of the values of the ligand field parameters for transition metals studied with corresponding literature data in aqueous media and some metal alkanoate melts [2-4] the following conclusions have been made. The cations Co (II) and Ni (II) most probably exist in octahedral ligand field in the decanoate mesomorphic melt, while the Cu(II) cations could have square-planar coordination environment.

It is found the molar absorptivities  $\epsilon_{\text{max}}$  for Co(II), Ni(II), Cu(II) cations in molten mesomorphic decanoate matrix depend on the cation potential of the matrix. They increase with decreasing cation potential that may reflects the tendency of enhancement of the coordination environment symmetry.

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## **Electrochemical synthesis of high pure tantalum oxide from molten salts**

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The production of high pure tantalum oxide is very interesting from practical point of view because of its valuable properties. Deposits which are produced in molten salt mixtures have ultra-fine structure. The molten mixture consists in chloride eutectic CsCl-NaCl with additions of sodium nitrate. Content of sodium nitrate varies from 0,1 to 30 mass %. Experiments were made in temperature range 800-900 K under argon atmosphere.

It is well known that tantalum can form oxide in molten nitrates. The main purpose of using of big amounts of chloride is to increase the temperature of oxidation and create a marked amount of nitrite ions in the melt because of decomposition of sodium nitrate at temperatures above 700 K. As it was shown in our experiments about 10% of initial nitrate can decompose to nitrite and oxygen at 800 K. Thus produced nitrite ions prevents of formation of dense good adhesive layers of tantalum oxide on its surfaces. X-ray analysis shows that thus formed oxide consists only from one phase and it is pure  $Ta_2O_5$ .

It was determined optimal regimes of formation pure fine tantalum oxide in molten mixture containing sodium nitrate under anodic polarization. Polarization curves looks like passivation ones but values of current density are too high.

## **Preparation and properties of glasses obtained by recycling of secondary lead from acid battery plants**

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The goal of our work is to study the chemical stability of harmless re-usable materials coming from the conversion of industrial wastes produced by a lead-battery plant.

The slag resulted from the thermal re-cycling of lead from spent batteries containing 5 to 10 %wt of Pb was vitrified with the necessary amount of silica and other additives in order to obtain the glasses with desired chemical stability.

We checked some recipes and operating parameters to elaborate the process leading to the samples studied here. These provided general conditions give the most convenient glass that was manufactured and characterized. In order to establish the chemical stability of the material, we study the influence of the composition on the structure and properties of the glass. The dependence of the glass on its environment is also tested.

The influence of composition and temperature on the structure of the glass will be discussed following the analysis of the data of the electrical conductivity experiments in solid and molten states. These data are correlated with the IR reflectivity spectra up to the melting point, MAS NMR and thermal analysis results.

The chemical stability tests were performed in different pH media and compared with those of the commercial glasses (Austria glass).

The obtained results are in good agreement with the commercial glass and after the improving of the process parameters this procedure will contribute to helping the battery plant deal with resources and wastes in a sustainable way.

# OXIDE SOLUBILITY AND STRUCTURAL PROPERTIES OF

## NdF<sub>3</sub> – LiF – MgF<sub>2</sub> - Nd<sub>2</sub>O<sub>3</sub> MELTS

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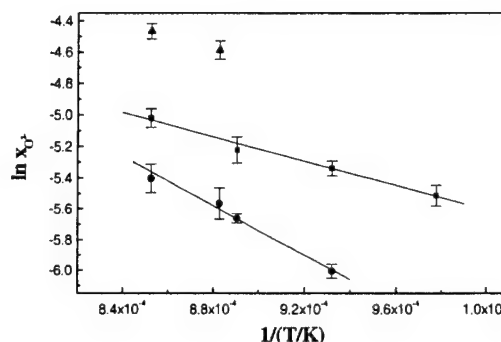
The solubility of Nd<sub>2</sub>O<sub>3</sub> in NdF<sub>3</sub> - LiF - MgF<sub>2</sub> melts is about 0.15 – 0.38 mole % when the NdF<sub>3</sub> concentration varies from 15 to 30 mole % at 900 °C. The solubility increases from 0.13 mole % at 750 °C to 0.22 mole % at 900 °C in the NdF<sub>3</sub> – LiF eutectic. The temperature variation of the oxide solubility is given by the equation:

$$\frac{d \ln x_{O^{2-}}^3}{d(1/T)} = - \frac{\Delta H_{ox}(s)}{3R}$$

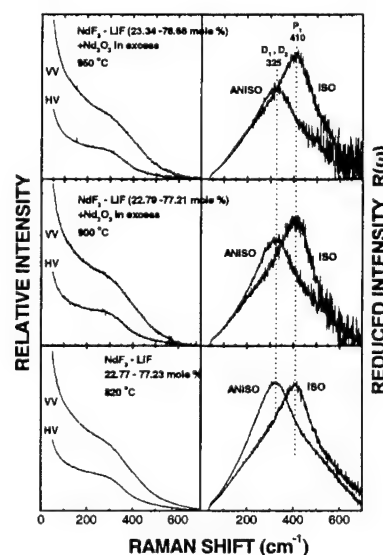
where, subscript *ox* stands for neodymium oxide. A plot of the natural logarithm of the O<sup>2-</sup> concentration versus 1/T yields straight lines (Fig.1) and  $\Delta H_{ox}(s) = \Delta_{fus} H_{ox}^0 + \Delta H_{ox}(liq) \approx 200 \text{ kJ}$  and 100 kJ for the 15 mole % and 23.1 mole % NdF<sub>3</sub> melts, respectively. Therefore, the partial enthalpy of mixing liquid Nd<sub>2</sub>O<sub>3</sub> into the NdF<sub>3</sub> - LiF binaries,  $\Delta H_{ox}(liq)$ , must be considerably positive. This is in agreement with the very low solubility measured.

When MgF<sub>2</sub> is added to NdF<sub>3</sub> – LiF binary melts saturated with Nd<sub>2</sub>O<sub>3</sub>, the Nd<sub>2</sub>O<sub>3</sub> solubility seems to decrease slightly at 30 mole % NdF<sub>3</sub>, while a slight increase was observed with 15 mole % NdF<sub>3</sub> in the binary. When dissolving Nd<sub>2</sub>O<sub>3</sub> in the NdF<sub>3</sub>-LiF eutectic, Raman spectroscopy shows that the complex ions NdOF<sub>x</sub><sup>(x-1)-</sup> and Nd<sub>2</sub>OF<sub>x+3</sub><sup>(x-1)-</sup> may form in the melt (Fig.2). The most reasonable candidate seems to be NdOF<sub>5</sub><sup>4-</sup>.

Electrochemistry studies of LiF-NdF<sub>3</sub>-MgF<sub>2</sub>-Nd<sub>2</sub>O<sub>3</sub> systems are also in progress and at present, a proper reference electrode is being constructed.



**Fig.1** Oxygen content,  $\ln(x_O)$ , plotted versus  $1/T$ . The LiF - NdF<sub>3</sub> melts investigated contained initially and ●: 15, ■: 23.1, ▲: 30 mol% NdF<sub>3</sub>,



respectively.

**Fig.2** Raman spectra of molten NdF<sub>3</sub> - LiF and NdF<sub>3</sub> - LiF - Nd<sub>2</sub>O<sub>3</sub> mixtures (Nd<sub>2</sub>O<sub>3</sub> in excess). The reduced representation of the isotropic and anisotropic spectra is depicted on the right side of the figure.

# The investigation of electrochemical production of Mg-Nd alloys from oxyfluoride media

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## 1. The determination of density

The density of the electrolyte and the Mg-Nd alloys was determined using hydrostatic weighing at certain temperature.

The Mg-Nd alloy density has determined in interval 20-1100°C for next compositions: 16.3; 23.0; 30.0; 45.8; 53.0; 70.0; 77.0 and 90.0% wt Nd.

In the interval 800-1100°C we have determined the melt density for system: LiF-NdF<sub>3</sub> and LiF-MgF<sub>2</sub>-NdF<sub>3</sub>. The experimental dates concerning the LoF-MgF<sub>2</sub>-NdF<sub>3</sub> melt density are presented in table.

Composition, % mass			Density, g/cm <sup>3</sup>	
LiF	MgF <sub>2</sub>	NdF <sub>3</sub>	800°C	950°C
50	40	10	2.225	2.145
50	35	15	2.222	2.124
50	30	20	2.231	2.162
50	25	25	2.274	2.240
50	20	30	2.375	2.314
50	15	35	2.333	2.274

## 2. Lab scale electrolysis of Nd<sub>2</sub>O<sub>3</sub> from fluoride melts on molten Mg-cathode

Experimental results confirm the creation of alloys Mg-Nd by thermo-chemical method (NdF<sub>3</sub> + Mg → 2Nd + 3MgF<sub>2</sub>) simultaneously with electrolysis. The current efficiency for Nd – 40.5%. The quantity of Nd obtained by electrolysis has defined how difference between quantity of Nd in alloys and Nd obtained by thermochemical reaction.

## 3. Lab scale electrochemical production of Mg-Nd alloys by co-deposition of Nd and Mg on solid cathode

Composition of electrolytes, % mass: NdF<sub>3</sub> – 63.5; LiF – 28.5; MgF<sub>2</sub> – 7.0. Feeding mixture: Nd<sub>2</sub>O<sub>3</sub> + MgF<sub>2</sub>. The results of electrolysis shown in table (Temperature 850°C).

No	Anodic current density A/cm <sup>2</sup>	Composition of anodic gas, % vol.			
		CO <sub>2</sub>	CO	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>
1.	0.186	30.2	46.8	12.2	10.8
2.	0.258	31.0	41.8	15.2	12.0
3.	0.387	24.7	38.8	16.9	19.6

The obtained alloys contains: Nd – 79.8; Mg – 20.2 % mass/

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## **The joint electroreduction of lanthanum, gadolinium and boron ions in chloride-fluoride melts**

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The joint electroreduction of lanthanum, gadolinium and boron ions in chloride-fluoride melts for realization of kinetic mode of synthesis of lanthanum and gadolinium double boride was investigated.

The change of general character of voltammetric dependencies (as cathodic, and anodic part) at introduction of borofluoride-ions concentration in chloride-fluoride melt, containing of lanthanum and gadolinium ions was occurred. The wave of borofluoride-ion reduction up to elementary boron was observed on katodic part of voltamograms at potentials  $-(1,3 \div 1,4)V$  rather platinum reference electrode in researched melt. The wave of joint electroreduction of lanthanum and gadolinium ions elongated along the potential axis into the more negative values. The increase of borofluoride-ions concentration lead to more change of cathodic wave form, the anodic wave especially. The waves which appropriated to individual dissolution processes is difficult to allocate on the cathodic part at it, and the dissolution of cathodic cycle product was occurred at much more positive potentials on anode part than in case of absence of fluoroborate-ions in melt. We assume that the formed product has semi-conductor conductivity proceeding from the form of voltamograms and the reduction of lanthanum with gadolinium is imposed on the process of boron reduction.

Thus, we think that the electrochemical synthesis of lanthanum and gadolinium double boride is possible only in kinetic mode, being based on the voltamograms analysis of chloride-fluoride melts.

Hence, the process of electrosynthesis of lanthanum and gadolinium double boride one can be presented as the following stages:

- reduction of a more electropositive component (boron);
- reduction of a more electronegative component (lanthanum and gadolinium) on previously deposited boron;
- mutual diffusion of lanthanum, gadolinium and boron leading to formation difference boride phases.

The received results of joint electroreduction can be used in practical realization of high-temperature electrochemical synthesis of lanthanum and gadolinium double boride.

## **ESR Study of Electron Localization and Dynamics in Metal-Molten Salt Solutions: Comparison of M-MX (M = alkali metal) and Re-ReX<sub>3</sub> Melts (Re = rare earth metal)**

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At elevated temperatures metals form true solutions with their molten salts over a wide composition range, whereby the electronic properties can vary from nonmetallic to metallic states. For understanding of the electronic structure of these solutions, the problem of electron localization and dynamics is of central interest. For solutions of monovalent metals strongly localized states like F-centers and bipolarons are discussed. In solutions of polyvalent metals like the Re-ReX<sub>3</sub> mixtures the situation is less clear. This is due to the fact, that various oxidation states with different stability are formed.

ESR gives valuable insight into the nature and dynamics of localized electronic states via the g-factor shift and the resonance line width. We have studied the ESR spectra in liquid K-KCl and M - NaCl/KCl<sub>eut</sub> (M = Na, K) mixtures at different concentrations in salt-rich melts approaching the M-NM transition region. In both systems F-center like characteristics are found. Strongly exchange narrowed signals clearly indicate electron dynamics on the ps scale. The ESR-spectra of Nd-NdCl<sub>3</sub> in (LiCl, KCl)<sub>eut</sub> are characterized by a large line width of  $\sim 10^3$  G decreasing with increasing temperature. The g-factor and correlation time are consistent with the model of intervalence charge transfer, which is supported by recent optical spectra. The different transport mechanisms will be discussed.

## Kinetics and Mechanism of the Magnesium Electrode Reaction in Molten $\text{MgCl}_2$ – $\text{LiCl}$ Binary Mixtures

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The kinetics and mechanism of the magnesium electrode reaction in six melts of the binary  $\text{MgCl}_2$  –  $\text{LiCl}$  system have been studied at several temperatures using electrochemical impedance spectroscopy (EIS) and a relaxation method with galvanostatic perturbation (RM). The electrode process was found to consist of three steps. A preceding chemical reaction is followed by two charge-transfer steps: the low-frequency one, showing mixed charge-transfer and diffusion character and a high-frequency one of pure charge transfer control. The highest densities of reaction current were determined to reach  $15 \text{ A cm}^{-2}$  at 1000 K for both electrochemical steps, varying with a melt composition. A mechanism of the overall electrode process in this system is proposed and determined data compared with those for other  $\text{MgCl}_2$  – alkali chloride systems.

## Studies on the Selective Transport of Organic Compounds using New Ionic Liquids as Supported Liquid Membranes

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Although known since the beginning of the XX century, only recently have room temperature ionic liquids (RTILs) attracted significant and growing interest, especially those based upon the 1-n-alkyl-3-methylimidazolium cation.<sup>[1,2]</sup>

They intrinsically hold useful properties such as high ionic conductivity, a large electrochemical window, negligible vapour pressure and thermal stability. Depending on the anion and alkyl group of the imidazolium cation, the RTIL may solubilize alcohols, alkyl halides, carbonyl compounds, supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and also transition- metal complexes. Simultaneously, they can have low miscibility with alkanes, water, dialkyl ethers and being insoluble in scCO<sub>2</sub>.<sup>[3]</sup>

A new series [C<sub>n</sub>O<sub>m</sub>mim][X] of imidazolium cation based room temperature ionic liquids (RTILs), with ether and alcohol functional groups on the alkyl side chain has been prepared.

In this work, we studied the possibility of using these new RTILs in bulk (non-supported) and supported liquid membranes for the selective transport of organic molecules.

A systematic selective transport study using 1,4-dioxane, propan-1-ol, butan-1-ol, cyclohexanol, cyclohexanone, morpholine and methylmorpholine, as a seven model component mixture of representative organic compounds; and two new RTILs [C<sub>n</sub>O<sub>m</sub>mim][X] which have been compared with four RTILs based on the 1-n-alkyl-3-methylimidazolium cation [C<sub>n</sub>mim][X] (n-butyl, n-octyl and n-decyl), with the anions PF<sub>6</sub><sup>-</sup> or BF<sub>4</sub><sup>-</sup>; immobilised in two different supporting membranes confirms that the combination of the selected RTILs with the supporting membranes is crucial to achieve a good selectivity for a specific solute.

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## Molecular Dynamics Study of Ionic Melts

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In our studies, we used an upgraded molecular dynamics (MD) simulation package to analyze the trajectories of individual particles. The equations of Newtonian mechanics were integrated to obtain the coordinates and velocity of each ion. Periodic boundary conditions were employed; at each time step, the system relaxed to thermal equilibrium. The initial velocities of the particles were set by a random number generator. MD simulations were carried out for temperatures between 400 and 1200 K at 50-K intervals.

By comparing simulation results with experimental data, the uncertainties in the position of the first and second PRDF (partial radial distribution functions) peaks were estimated to be 8 and 15% respectively. The uncertainty in diffusion coefficients was 15%, and that in the velocity autocorrelation function was 9%.

The properties of the melt were determined above the contact-melting temperature, which was evaluated from the jump in the diffusion coefficient.

The results show that, in the systems with a common anion, the diffusion coefficients of the cations increase and that of the anion decreases as the size of the anion rises. The height of the first PRDF peak increases with decreasing anion radius. The interionic distances in the melt increase with anion size.

In the systems with a common cation, the diffusion coefficient of the cation rises as size of the second anion increases, while the heights of the PRDF peaks are inversely related to the size of the second anion.

EFFECT OF THE IONIC COMPOSITION ON THE FORMATION OF THE  
ELECTROCHEMICAL ACTIVE SPECIES OF NIOBIUM IN FLUORIDE MELTS ON THE  
BASE OF RAMAN SPECTROSCOPIC STUDIES

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For the increase of the efficiency of the existing industrial process and for the development of new technologies of refractory metals deposition from molten electrolytes, the formation and stability of electrochemically active species, their transport to the electrodes and the mechanism of electrode reactions have to be studied.

The presence of oxides in molten electrolytes used for formation of anticorrosive niobium coatings either as impurities or as additives affect favorably the quality of the coatings. The ionic composition of the electrolyte influences directly on the formation of its electrochemical active components and has a dramatic influence on the deposition process because all refractory metals exist in a variety of oxidation states. The stability of the lower oxidation states of the refractory metals depends on the electrolyte composition: lithium ions stabilize the lower oxidation states. When the better ligand donors such as potassium, sodium or cesium are used, the higher oxidation states become more stable. This trend is more pronounced when a stronger ligand such as fluoride ions is used.

The formation of the electrochemically active species of niobium in molten fluoride melts ( $\text{LiF-NaF-K}_2\text{NbF}_7\text{-Na}_2\text{O}$  and  $(\text{NaF-KF})\text{-K}_2\text{NbF}_7\text{-Na}_2\text{O}$  at the different ratio  $\text{O}^{2-} : \text{Nb(V)}$ ) were studied by means of the Raman spectroscopy at the temperature 780-800°C. The obtained results are compared with the Raman spectra of the molten system  $\text{FLiNaK-K}_2\text{NbF}_7\text{-Na}_2\text{O}$ , where three alkali metals are present. The influence of the alkali metal cations on the chemical behavior of the niobium in the fluoride melts and on the peculiarities of the formation of the oxofluoride niobium species are discussed.

#### Acknowledgments

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## A SPECTROSCOPIC INVESTIGATION INTO TECHNETIUM AND RHENIUM SPECIATION IN CHLORIDE MELTS

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High temperature alkali metal chloride-based melts are prospective reaction media for pyrochemical reprocessing of spent nuclear fuels. In current PUREX (plutonium and uranium recover by extraction) process operations Tc is one of the few fission products that forms an anionic species ( $\text{TcO}_4^-$ ) making its control more challenging than most of the other major fission products. Despite the unusual properties of Tc in aqueous/extraction process there is only limited information available on its behaviour in chloride melts.

Initially we studied rhenium (a technetium analogue) speciation in selected chloride based melts to develop the methodology. However, as Tc has significantly different red-ox chemistry it was also necessary to study the speciation of this radioactive element directly.

Rhenium-containing melts were prepared by reacting rhenium metal, dioxide or trioxide with chlorine or hydrogen chloride in a chosen chloride mixture and also by anodic dissolution of rhenium metal. Technetium was introduced into the melts by reacting technetium dioxide (obtained by thermal decomposition of ammonium pertechnetate) with hydrogen chloride or chlorine. The progress of the reactions was followed by *in situ* absorption spectroscopy measurements. The experiments were conducted in the melts based on LiCl-KCl eutectic, NaCl-CsCl eutectic and NaCl-KCl equimolar mixture, in the temperature range 450 to 720 °C. The chlorination reaction was conducted in standard 1 cm high-temperature spectroscopy cells. The uv/viz/nir absorption spectra were measured *in situ* between 200 and 1100 nm using a custom built set up based on a Ocean Optics SD2000 fibre optic spectrophotometer. The spectra of technetium species in molten salts are reported here for the first time. The additional information on the speciation of technetium and rhenium was obtained from the analysis of quenched melts by available spectroscopic techniques including EXAFS, IR and Raman spectroscopy. The mean oxidation state of studied metals was determined by oxidimetric analysis.

According to the spectroscopic characterisation of both the molten salt and quenched melts the reaction of rhenium metal and dioxide with both hydrogen chloride and chlorine results in the formation of stable rhenium(IV) complexes,  $\text{ReCl}_6^{2-}$ . Technetium dioxide reacts with hydrogen chloride also producing stable hexachlorocomplex,  $\text{TcCl}_6^{2-}$ . Reaction of  $\text{TcO}_2$  with chlorine however surprisingly results in partial oxidation of technetium to  $\text{TcO}_4^-$  which is retained in the melt, and some technetium is lost as a volatile chloride.

# INDUCED MESOPHASES IN BINARY MELTS BASED ON CAESIUM BUTANOATE

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Some organic salts are known to have latent (virtual) liquid crystalline properties that can show up in binary systems due to the melting temperatures in them becoming lower than the latent mesophase clearing temperatures [1-3]. Among these salts is caesium butanoate [1].

In the present work the phase diagrams of the binary systems of caesium butanoate with magnesium, calcium, strontium and barium butanoates have been studied in order to discover the formation of induced liquid crystalline phase and determine the composition ranges of mesophase and glass existence. Pure Mg, Ca, Sr and Ba butanoates (But) do not form liquid crystals but supercool and form glasses easily under cooling their liquid phases. Pure CsBut does not form either the mesophase or glass but has the latent mesomorphic properties.

The complete T-x diagrams of binary systems have been constructed on the basis of DTA and polythermal polarization microscopy data.

System  $x\text{CsBut} + (100-x)\text{MgBut}_2$  (I). There exists a congruently melting complex. No liquid crystals have been obtained in the system. Optical isotropic glasses may be observed in the range  $0 \leq x \leq 30$  mol%.

In the systems  $x\text{CsBut} + (100-x)\text{CaBut}_2$  (II), or  $\text{SrBut}_2$  (III), or  $\text{BaBut}_2$  (IV), the intermediate homogeneous liquid crystalline solutions, identified as smectic A, are formed (table 1). All systems are characterised by the formation of several congruently (D) and incongruently (P) melting complexes. Glass formation has been observed in all these systems in wide composition ranges ( $0 \leq x \leq 80$  mol%), but only in the systems III and IV vitreous mesophases have been obtained.

**Table 1**

*Induced mesophase characteristics in binary systems of caesium and alkali-earth metal butanoates*

Binary system	Mesophase formation range, x, mol%	Maximum $T_{\text{clearing}}$ , °C	Mesophase type	Complex composition, x, mol%
$x\text{Cs} + (100-x)\text{Mg} \mid \text{But}$ (I)	0	no	no	40 (D)
$x\text{Cs} + (100-x)\text{Ca} \mid \text{But}$ (II)	$79 < x < 86$	293	smectic A	20 (P), 75 (D)
$x\text{Cs} + (100-x)\text{Sr} \mid \text{But}$ (III)	$60 < x < 88$	300	smectic A	50 (D)
$x\text{Cs} + (100-x)\text{Ba} \mid \text{But}$ (IV)	$44 < x < 88$	326	smectic A	33 (D), 80 (P)

It is found that the concentration and temperature range of induced mesophase in binaries with CsBut is the greater, the larger the alkali-earth metal radius ( $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$ ). Moreover formation of complexes with high content of CsBut in binaries II-IV favours the exhibition of latent mesophase of CsBut.

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# ELECTRODEPOSITION OF RHENIUM ON MONOCRYSTALLINE STRAIGHT AND BENT RHENIUM SUBSTRATES FROM MOLTEN SALTS

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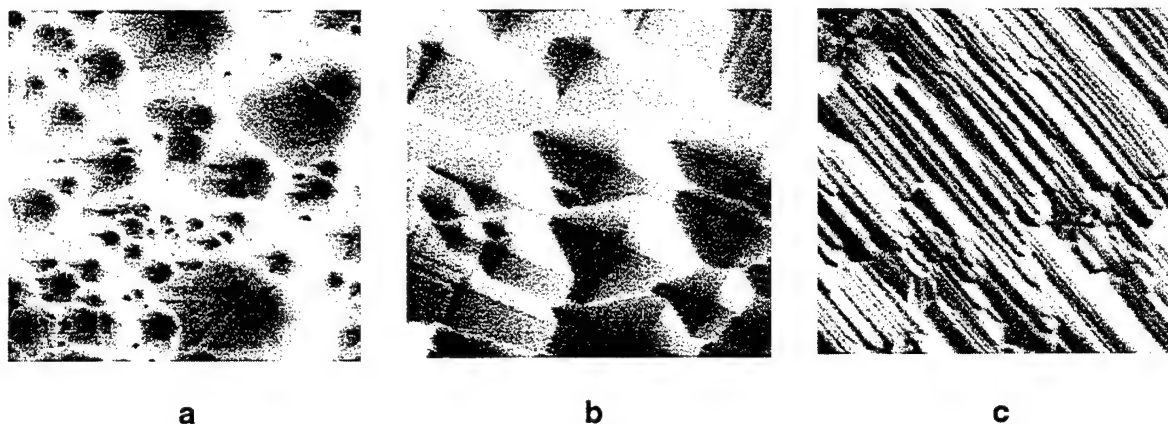
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The experiments were carried out in molten mixture of cesium and rhenium chlorides in the range of cathodic current density  $0.02-0.10 \text{ A/cm}^2$  at temperature  $870^\circ\text{C}$  in inert atmosphere. The straight and bent monocrystalline rhenium plates with orientations  $(10\bar{1}0)$ ,  $(11\bar{2}0)$ ,  $(0001)$  were used as cathode materials. The structural perfection and the surface morphology were investigated by X-ray diffraction, metallographic and opticogoniometric methods with the help of optical microscope "Neophot-32" and SEM "Camebax".

It was established that the rhenium deposits on the compact graphite substrate had usually the  $(10\bar{1}L)$  growth texture where  $3 \leq L \leq 5$ . In this case the epitaxial growth onto the rhenium monocrystalline substrate with  $(0001)$  orientation was occurred but the epitaxial growth was broken up on the substrates with  $(11\bar{2}0)$  and  $(10\bar{1}0)$  orientations and the formation of the  $(10\bar{1}L)$  growth texture began. If the growth texture of the rhenium deposits on the graphite was absent the epitaxial growth on the rhenium substrates with the orientations  $(0001)$  and  $(11\bar{2}0)$  took place.

The surface morphology of the rhenium deposits on the straight and bent substrates was identical. It was established that epitaxial growth proceeded layer by layer by a two-dimensional mechanism. The main morphological features of single crystal rhenium deposits were the growth pits with a symmetry corresponding to the symmetry of monocrystalline substrates (Fig.1a,b) or the growth steps (Fig.1c)

It was established that relative growth rate anisotropy in the various directions took place. The relative growth rate of rhenium deposits on the  $(0001)$  substrate was larger than on the  $(11\bar{2}0)$  and  $(10\bar{1}0)$  ones at  $i_c = 0.05 \text{ A/cm}^2$ .



**Fig.1.** Surface morphology of epitaxial rhenium deposits on single crystal rhenium substrates with orientations: (a) –  $(0001)$ ; (b)  $(11\bar{2}0)$ ; (c) –  $(10\bar{1}0)$ . X2000

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## **Development of electrochemical separation methods for Molten-Salt Reactor fuel processing**

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Molten-Salt Reactors are considered to be one of the very promising advanced nuclear reactor systems providing sustainable development of nuclear energy in the near future. The main advantage of Molten-Salt Reactor systems, based on the use of liquid nuclear fuel in the form of molten fluoride salts, is the integration of nuclear reactor with the nuclear fuel processing and consecutively spent fuel reprocessing systems. This integration permits to return the dangerous long-lived transuranium elements immediately back in the reactor core for their transmutation into short-lived fission products or even to stable isotopes. The Molten-Salt Reactors with molten fluoride salt fuel could be applied as the typical transmutation systems, burning of plutonium and other transuranium elements from the spent fuel of contemporary reactor types or as the advanced power reactors working under the thorium - uranium fuel cycle with the minimized production of long-lived transuranium wastes.

The electroseparation methods are in the focus of interest for the whole area of Molten-Salt Reactor fuel cycle. The main goal of these methods is partitioning of actinides from lanthanides.

The paper is concentrated to the development of electrochemical partitioning method of uranium and selected lanthanides from molten fluoride salt media. The melt used at present is ternary eutectic mixture of lithium, sodium and potassium fluorides (so-called FLINAK – 42.0 % KF, 46.5 % LiF, and 11.5 % NaF (in molar %)) with the melting point at 454 °C. The methods for conditioning of the materials before melting are discussed.

The experimental set-up for measurement of electrochemical properties is described with emphasis put on material selection both for construction material for electrolyser and electrodes, as well as the development of reference electrode design for measurement in molten fluoride salts. The measured data concerning uranium and neodymium are presented and electrochemical behaviour of these elements in molten fluoride salts is discussed.

## Study of Carbon Nucleation in Molten Fluorides

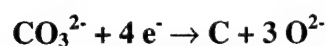
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### Abstract

In a previous work [1], we had stated that amorphous carbon can be prepared by electrochemical reduction of carbonate ions  $\text{CO}_3^{2-}$  dissolved in a molten LiF-NaF mixture, in a one-step process, in the 700-800°C temperature range:



In the present work, the electrochemical nucleation of carbon in molten alkaline fluoride media was investigated using cyclic voltammetry, chronopotentiometry and chronoamperometry in the 670-750°C temperature range.

The objective is now to get data on the phenomena involved in the initial phase of electrolytic deposition in order to optimise a strategy for the preparation of carbon coatings. We will investigate the nucleation phenomenon and the initial growth of the carbon nuclei on a gold electrode, using the chronoamperometry of electrolyte at low concentration. Plotting our experimental results will be compared with the theoretical one for each nucleation mode: instantaneous and progressive. Then, the influence of the temperature and the overvoltage on the nucleation mode and on the number of nuclei generated will be examined.

According to our experimentations, the deposition process involves progressive nucleation with diffusion-controlled growth of the nuclei, and scanning electron microscopy shows that the shape of the nuclei is hemispherical.

[1] : L. Massot, P. Chamelot, F. Bouyer and P. Taxil, *Electrochimica Acta*, **47**, 1949-57 (2002).

## Neodymium electrodeposition process in molten fluoride media.

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This work concerns the neodymium extraction in molten fluoride media by electrodeposition and more particularly the examination of various solvents and working electrode (solid and liquid), reliable for this process.

Experiments have been carried out on two types of working electrode: Mo and Ni. Mo does not give alloys with Nd whereas Ni-Nd alloys or compounds are predicted by the binary phase diagram.

For a same working electrode, the reduction of the solvent ions defines the cathodic limit of the electrochemical window of the electrolyte. Results providing from cyclic voltammograms in our works concerning the scale of the reduction potentials of the alkaline cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) are in agreement with thermodynamics data.

Experiments in LiF-NaF and LiF-KF media at respectively 700°C and 500°C did not allow the formation of neodymium alloys or neodymium deposit to be identified: no reduction waves of Nd ions were observed in the cyclic voltammograms on Mo or Ni at these temperatures.

Then, the electrochemical behaviour of LiF-NdF<sub>3</sub> at 880°C was investigated by cyclic voltammetry. Neodymium fluorides are reduced at a potential close to the solvent reduction on Mo cathode in a one step process exchanging three electrons and gives Nd<sup>(0)</sup> [1]. We observed a linear relationship between the reduction peak current density with both the NdF<sub>3</sub> content and the square root of the scan rate, showing that the reaction is controlled by the diffusion of electroactive species in the melt. On a Ni cathode, the reduction wave is more anodic and the same features concerning the variation of current density were observed than before. Electrolyses at the potential previously defined yields an homogeneous liquid alloy Ni-Nd.

After sodium and potassium fluoride addition (respectively 3.8 wt% and 2.2 wt%) in LiF melt at 880°C, the reduction wave of sodium and potassium on a Mo cathode hides the reduction peak of neodymium fluoride. So the Nd metal deposition is hindered by the reduction of the solvent ions ( $\text{Na}^+$  and  $\text{K}^+$ ). Nevertheless the alloy's characteristic wave is still observed on Ni cathode.

So we conclude that the neodymium can be extracted using a nickel cathode by electrolysis of LiF-NdF<sub>3</sub> mixture at 880°C and higher temperature and by electrolysis of LiF-NaF-NdF<sub>3</sub> and LiF-KF-NdF<sub>3</sub> mixture at 880°C in the form of liquid alloy Nickel Neodymium.

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# Neutron Diffraction Study of Ionic Aggregation in Lead Halide Melts

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In general, rare earth elements become trivalent cations and form stable compounds, but Eu, Sm, and Yb are known to be stable also in divalent states. In order to deduce the structure of divalent rare earth halide melts, it is effective to substitute, for example,  $\text{EuCl}_2$  melt for  $\text{PbCl}_2$  and  $\text{PbBr}_2$  melts because of difficulty in sample preparations. The structure of  $\text{PbCl}_2$  melt has so far been investigated by Raman spectroscopy [1-3], X-ray diffraction [4, 5], and EXAFS [6], indicating that there exist complex species such as  $[\text{PbCl}_3^-]$ ,  $[\text{PbCl}_4^{2-}]$ ,  $[\text{PbCl}_6^{4-}]$ , and so on. Unfortunately, a large scattering of findings are reported in the previous works mentioned before. In this work, pulsed neutron diffraction experiments of  $\text{PbCl}_2$  and  $\text{PbBr}_2$  melts were preliminarily carried out for the identification of ionic species and the structural analysis of coordination shell.

The reagent grade chemicals  $\text{PbCl}_2$  and  $\text{PbBr}_2$  were dehydrated in a usual manner. The densities of the melts were measured by using the dilatometer made of fused silica. The pulverized salt sample was introduced into the transparent fused silica cell and the scattered neutron intensities were measured after melting by the time-of-flight method and then corrected in the conventional way. Neutron scattering experiments were performed using the High Intensity Total scattering spectrometer (HIT- $\square$ ), which is designed to measure the structure factor  $S(Q)$  at high rate of data collection over a wide range of momentum transfer  $Q$  (from 0.5 to  $40\text{\AA}^{-1}$  in this work) and installed in the pulsed neutron source of High Energy Accelerator Research Organization, Neutron Science Laboratory at Tsukuba, Japan.

According to the radial distribution analysis of  $\text{PbCl}_2$  melt, the Cl-coordination numbers around Pb were found to be about 4, corresponding to the peak at  $r = 2.84\text{\AA}$  in  $G(r)$ , and to be about 2 at  $r = 3.40\text{\AA}$ , respectively. These two peaks were thought to form the first coordination shell. On the contrary, the Br-coordination number around Pb was estimated at about 4. Although  $\text{PbCl}_2$  and  $\text{PbBr}_2$  have the same crystal structure, it was of much interest that the short-range structure of the melts was quite different from each other.

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**Use of room-temperature ionic liquids for nuclear waste reprocessing : preliminary studies**

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The physical and chemical properties of actinide and lanthanide elements in room-temperature ionic liquids offer several advantages with respect to classical hydrometallurgical separations in use for elements produced in the nuclear fuel cycle.

We are investigating the structural properties of  $\text{UO}_2^{2+}$  and  $\text{Eu}^{3+}$  in a limited series of room-temperature ionic liquids of the Bumin type (1-butyl-3-methylimidazolium cation), with the anions  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $\text{PF}_6^-$  and  $\text{BF}_4^-$ . These first two Bumin-anion systems have been selected on the basis of their interesting properties for liquid/liquid extraction of radionuclides that have been already demonstrated. The last system is chosen for the sake of comparison, as more physical-chemical basic properties are known for this specific liquid.

Preliminary results on the potentialities of these liquids will be presented such as solubilities of various U(VI) and Eu(III) salts, electrochemical and liquid/liquid extraction properties. The influence of various impurities on these parameters will be discussed. Time-Resolved Laser-induced Fluorescence Spectroscopy is performed in typical solutions, as this technique yields some information on the number and type of ligands around the central ion ( $\text{UO}_2^{2+}$  or  $\text{Eu}^{3+}$ ). In this case, comparison of  $\text{UO}_2^{2+}$  complexation with the  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $\text{PF}_6^-$  and  $\text{BF}_4^-$  ions in water will be made.

**Spectroscopic investigation of the structural properties of the  
LnI<sub>3</sub>-AI (Ln=Dy, Ho and A=Cs, Na) binary systems**

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**ABSTRACT**

The structural and thermodynamic properties of molten trivalent metal halides and their binary compounds with alkali halides depend strongly on the physicochemical properties of the trivalent salt. Studies of binaries containing high-melting lanthanide iodides are limited, mainly due to experimental difficulties. The practical interest for studying these mixtures arises from their use as additives in high-intensity-discharge mercury lamps.

In the present work, a Raman spectroscopic investigation of the LnI<sub>3</sub>-AI (Ln=Dy, Ho and A=Cs, Na) binary systems is presented. Composition and temperature dependence of the Raman spectra of the molten mixtures have been obtained. The changes of the vibrational modes upon melting the Cs<sub>3</sub>LnI<sub>6</sub> and Cs<sub>3</sub>Ln<sub>2</sub>I<sub>9</sub> (Ln=Dy, Ho) binary compounds have also been measured by recording Raman spectra of both the solids and corresponding melts from 25 °C up to temperatures above their melting points. The data are discussed in terms of the liquid phase structure.

## DEPENDENCE OF THERMAL CONDUCTIVITY IN MOLTEN SALTS ON PACKING FRACTION

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Since many errors are caused by thermal radiation, convection and intrinsic properties of molten salts such as corrosiveness and ionic conductivity, accurate determination of thermal conductivity is extremely difficult for molten salts at high temperature. Molecular dynamics (MD) simulation is useful for the evaluation of thermal conductivity of molten salts since it is free from such experimental difficulties. Moreover, it enables us to investigate the dependence of thermal conductivity on each thermodynamic variable such as temperature and density.

So far, we have evaluated the thermal conductivity of a series of molten alkali halides using MD simulation and the Green-Kubo technique. The obtained results are in quantitative agreement with experimental ones. In addition, it was found that the calculated thermal conductivity depends not on temperature but number density[1]. Furthermore, we investigated the mass dependence for some molten alkali halides. In addition, the phonon velocity of longitudinal optic mode was evaluated from charge-charge dynamic structure factors for these melts as a function of ionic mass. These results showed that the thermal conductivity is directly affected by ionic mass and is directly proportional to the phonon velocity in the same way as insulating solids.

In the present study, we examined the dependence of thermal conductivity of some molten alkali halides on packing fraction,  $\eta$ . The results showed the thermal conductivity is proportional to  $\eta^{2/3}$ . A plot of a series of calculated thermal conductivity as a function of number density, ionic mass and packing fraction shows good linearity.

[1] K. Takase, T. Oono, I. Akiyama and N. Ohtori, EUCHEM Conference on Molten Salts, 2000.



## RAMAN STUDY OF SODIUM AND IRON DOUBLE OXIDES AT HIGH TEMPERATURE

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Sodium oxides react with iron and form several kinds of double oxides at high temperature. Since it has been recognized that liquid metal sodium can damage the structures when it leaks under the atmosphere in the fast breeder reactor, the behavior of sodium in the atmosphere has extensively been studied. We have applied Raman spectroscopy to the analysis of reaction products as a method of identification at high temperature. Raman spectroscopy has potentials in two ways: the detection of highly corrosive chemical species such as peroxide or superoxide ions in the melts and the identification of corrosion products such as some kinds of sodium iron double oxides. In the previous study, we reported the possibility of the detection of peroxide and superoxide ions in molten sodium hydroxide[1].

In the present study, we first performed the measurements of Raman spectra for a series of sodium iron double oxides,  $\alpha$ -NaFeO<sub>2</sub>,  $\beta$ -NaFeO<sub>2</sub>, Na<sub>4</sub>FeO<sub>3</sub>, Na<sub>5</sub>FeO<sub>4</sub> and Na<sub>3</sub>FeO<sub>3</sub>, at room temperature in order to clarify the usefulness as a method of identification. The obtained characteristic spectra showed the possibility of qualitative identification for main components. We next tried to measure the spectra at elevated temperature for the purpose of examining the applicability of the method at high temperature such that the corrosion reaction occurs. Although the spectra have been successfully obtained for all double oxides up to 573K, these could not have been obtained for some oxides such as Na<sub>4</sub>FeO<sub>3</sub> and Na<sub>5</sub>FeO<sub>4</sub> at higher temperature. In the present report, we also discuss the origin of the barrier and present the results of the application of UV laser as a light source to the spectroscopic method in order to evade it.

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**Structural investigation of vanadium – sodium metaphosphate glasses, using solid-state NMR and Raman spectroscopy**

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**ABSTRACT**

Vanadium phosphates are interesting materials due to their catalytic and magnetic properties. The knowledge of their local structure is necessary to design materials having desired properties. In condensed phosphates, phosphorus always occurs in tetrahedral coordination. The phosphate network is made of PO<sub>4</sub> groups linked together to form dimers, chains, rings or cages, depending on composition. The size and valence of the adjacent cations and the length of the phosphate linkages determine the geometric parameters of each PO<sub>4</sub> group. In contrast, vanadium(V) into an oxygen environment has the tendency to form various V<sup>V</sup>O<sub>x</sub> polyhedra (VO<sub>4</sub>, VO<sub>5</sub>, VO<sub>6</sub>) with the characteristic V=O group.

In this work, we have investigated the glass forming system: (V<sub>2</sub>O<sub>5</sub>)<sub>x</sub> - (Na<sub>2</sub>O·P<sub>2</sub>O<sub>5</sub>)<sub>(1-x)</sub> (where x=0–0.5). The structural modifications of the sodium phosphate 'network' upon addition of different amounts of vanadium(V) oxide are characterized using multinuclear solid-state NMR and Raman spectroscopy. The <sup>31</sup>P MAS NMR spectra allow to evidence distinct PO<sub>4</sub> tetrahedra that can be assigned to Q<sub>2</sub>, Q<sub>1</sub> and Q<sub>0</sub> units. Both the evolution of the Q<sub>n</sub> relative intensities and the frequency shift of the main phosphorus-oxygen Raman bands reflect the depolymerization of the phosphate network upon the addition of V<sub>2</sub>O<sub>5</sub>, which results to the formation of VO<sub>x</sub> polyhedra. In addition, <sup>51</sup>V MAS NMR indicates the presence of both VO<sub>4</sub> and VO<sub>5</sub> units connected to PO<sub>4</sub> tetrahedra in the glass network.

**Acknowledgement**

AC wish to acknowledge the financial support from the University de Pau et des Pays de l'Adour. AC, FF and DM acknowledge financial support by European Community contracts HPRI-CT-1999-00042.

# ELECTRODE PROCESS IN $(\text{KCl-KF})_{\text{eut.}}$ - $\text{Gd}_2\text{O}_3$ HALIDE MELT.

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Rare earth metals (REM) cannot be produced from aqueous solutions due to their high reactivity. Electrolysis brings about the formation of hydrate oxides at the cathode, so that even using a mercury electrode results in the formation of a water-decomposed amalgam. For this reason, REM are produced by electrochemical methods not from aqueous solutions but from molten salts. At the same time, REM alloys were earlier produced by pyrometallurgical methods providing a simultaneous reduction from oxides, while molten salt electrolysis has come into practice only recently and requires further study. The reported evidence on gadolinium reduction from halide salt melts is not abundant and often contradictory. The melts used by the researchers usually contained oxygen either in the form of impurities (arising from the use of oxygen-containing ceramics in contact with the melt) or due to gadolinium oxide dopants, which seriously affect both the cathode reactions and deposit morphology, while the formed oxofluorides distort the calculated kinetic parameters. It is still important to select the correct background melt for studying the electrochemical behaviour of gadolinium complexes and for electrodeposition of gadolinium metal.

Studying of the electroreduction of gadolinium ions from KCl-KF eutectic melt at 1023K doped with gadolinium oxide (0.039-0.22 mole %) at glassy carbon and molybdenum electrodes has shown that the electrochemical response of the system reflects a one-stage character of the process with a transfer of three electrons as the result of the following reactions:



Reaction (1) is chemical dissolution of the gadolinium oxide dopant in the melt. Reaction (2) is reduction of the oxofluoride complex with Gd(III) at a cathodic polarization of the electrode. Analysis of the voltammetric dependencies according to the criteria of linear voltammetry determined the process (2) as reversible followed by a reversible chemical reaction of interaction of cathodic gadolinium with the melt, presumably the following composition:



Cyclic voltammograms recorded a significant difference between the cathodic and anodic peak potentials and cathodic current peak values greater than the anodic ones. Such ratios could have resulted from different rates of reactions (2) and (3). Provided the reaction (3) is fast and (2) slow, the ratio of cathodic and anodic process peak currents is explicable, the delay of anodic process probably accounted for by the dissolution of not gadolinium metal but the oxofluoride formed as the result of reaction (3).

Studies of the process at the molybdenum electrode relatively a glassy carbon reference electrode have revealed the presence of an ascending initial section preceding the reduction peak of the gadolinium-bearing complex. This section coincided with the corresponding area of the voltammogram of the background electrolyte and corresponded to the onset of reduction at the alkaline metal cathode. Its current power did not depend on the concentration of gadolinium oxide introduced to the melt, which corroborated the assumption of a process unassociated with the reduction of any oxygen-bearing gadolinium ions.

Calculation of the diffusion coefficient for three-valent gadolinium incorporated in an oxofluoride complex at 1008K and gadolinium oxide concentration in the melt equal to  $9.506 \cdot 10^{-5} \text{ mol} \cdot \text{cm}^{-3}$  yielded the value  $9.346 \cdot 10^{-5} \text{ cm} \cdot \text{s}^{-1}$ , which is higher than the known values reported by other researchers for chloride melts. The strength of fluoride-containing gadolinium

complexes being higher than with chloride-containing ones, such a high value of the diffusion coefficient can be explained by the reduction in both the near-electrode layer and binary electrical layer of oxofluoride gadolinium complexes by potassium metal, the beginning of which reduction was recorded at the molybdenum electrode:



Reactions (1), (2), (3) and (4) considerably complicate the interpretation of the processes and the application of known dependencies for calculation of the number of electrons participating in the process of gadolinium-containing complex reduction.

The linear increase of the wave of oxide-ions oxidation at anodic voltammograms (the working electrode – glassy carbon, quasireference electrode – molybdenum) with the  $\text{Gd}_2\text{O}_3$  content in the melt suggests a complete dissolution of gadolinium oxide in the studied temperature range.

Galvanostatic electrolysis at molybdenum and glassy carbon electrodes at a current density corresponding to the gadolinium oxofluoride complex reduction potential results in the formation of dark deposits at the cathode. Analysis of the diffractograms has shown the presence in  $(\text{KCl-KF})_{\text{eut}} - \text{Gd}_2\text{O}_3$  melt of a compound isostructural of  $\text{EuOF}$ , which is apparently nothing but  $\text{GdOF}$ .

The author is grateful to the Russian Academy of Sciences (project “High temperature chemical and electrochemical synthesis of new compounds on the base of rare and rare-earth metals) for the financial support of this study.

**JOINT ELECTROREDUCTION OF GADOLINIUM AND BORON**

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Gadolinium borides (especially hexaboride) are attractive due to their high emission characteristics. Up to now the hot pressing and plasma arc fusion are the main methods of Rare Earth Metal borides production. Herein we estimate the possibilities of High temperature electrochemical synthesis in their producing.

We investigated the joint electrodeposition of boron and gadolinium in chloride-fluoride melt (the most interesting from technological point of view) with the voltammetric methods on Molybdenum and Silver indicating electrodes.

Individual electrodeposition of Gd and Boron is reported in literature [1-3]. Both elements reduce from chloride-fluoride melts in one irreversible step. Complex shape of electrolyte-KBF<sub>4</sub>-GdF<sub>3</sub> voltammograms reflects the formation of a number of compounds which is in agreement with phase diagram [4]. However X-Ray phase analysis of the product of potentiostatic electrolysis at potential of the most negative peak proves the monophase GdB<sub>6</sub>-electrodeposition.

**Acknowledgement**

The authors are grateful to Russian Academy of Sciences (project High temperature chemical and electrochemical synthesis on new compounds on the base of rare and rare-earth metals) for the financial support of this study.

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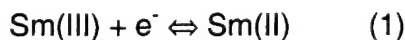
# INTERVALENCE CHARGE TRANSFER OF COUPLES Eu(III)/Eu(II), Sm(III)/Sm(II) AND Yb(III)/Yb(II) IN AN EQUIMOLAR MIXTURE OF MOLTEN NaCl-KCl

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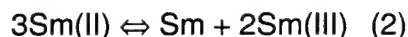
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The electrochemistry of redox couple Eu(III)/Eu(II) in details was investigated previously in [1, 2]. The present studies report the electroreduction-electrooxidation process



in NaCl-KCl melt in the temperature range 973-1123 K on glassy carbon, molybdenum, and tungsten electrodes studied by different electrochemical methods including cyclic voltammetry, chronopotentiometry and impedance spectroscopy. The results show that at a polarisation rate  $v < 0.3 \text{ V s}^{-1}$  the process of electroreduction of Sm(III) to Sm(II) is complicated by the disproportionation reaction (DPP)



At polarisation rate  $v \geq 0.3 \text{ V s}^{-1}$  influence of the DPP reaction is found to be negligible and the electroreduction process proceeds mostly under diffusion control. The diffusion coefficients ( $D$ ) of Sm(III) and Sm(II) determined by linear sweep voltammetry, chronoamperometry and chronopotentiometry methods show that the  $D$  decreases with increase in the oxidation state of samarium, while the activation energy for diffusion increases.

The standard rate constants ( $k_s$ ) for the reaction (1) were calculated on the basis of cyclic voltammetry and impedance spectroscopy data. The preliminary results on electrochemistry of redox couple Yb(III)/Yb(II) were also obtained. On the basis of the data obtained it is possible to conclude that in NaCl-KCl melt

$$D_{\text{Sm(III, II)}} > D_{\text{Eu(III, II)}} > D_{\text{Yb(III, II)}}$$

$$k_s^{\text{Sm}} > k_s^{\text{Eu}} > k_s^{\text{Yb}}$$

## Acknowledgements

The author<sup>1</sup> is grateful to the University of Provence (I.U.S.T.I., 13453 Marseille, France as well as the Russian Academy of Sciences (project "High temperature chemical and electrochemical synthesis of new compounds on the base of rare and rare-earth metals") for the financial support for this study.

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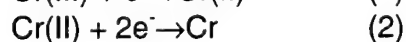
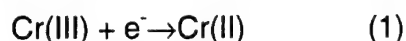
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# ELECTROCHEMISTRY AND ELECTROREFINING OF CHROMIUM IN CHLORIDE AND CHLORIDE-FLUORIDE MELTS

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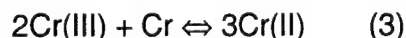
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The electroreduction of  $\text{CrCl}_3$  in NaCl-KCl equimolar mixture has been studied in the temperature range 973-1123 K by cyclic voltammetry and chronopotentiometry. The electrochemical reduction of Cr(III) in NaCl-KCl melt occurs *via* two successive reversible stages involving transfer of one and two electrons:



Investigation of the influence of fluoride ions additions (NaF) on the electrochemical processes (1) and (2) reveals that in chloride-fluoride melts, although the first stage remains reversible, the second becomes irreversible and is controlled by the electron transfer. Different kinetic parameters of chromium electroreduction were determined.

The formal standard potentials  $E^\circ_{\text{Cr(II)/Cr}}$ ,  $E^\circ_{\text{Cr(III)/Cr}}$ , and formal standard redox potentials  $E^\circ_{\text{Cr(III)/Cr(II)}}$  determined from linear sweep voltammetry data were used to calculate the equilibrium constants of metal-salt reaction:



The calculated values of the equilibrium constants indicated that in the presence of metallic chromium, only complexes of Cr(II) exist in the chloride and chloride-fluoride melts.

The comparative study of electrorefining of aluminothermic chromium in pure chloride and chloride-fluoride melts shows that the use of chloride melt should be preferable. The content of Fe, V, Co and Ni in the electrolytic chromium is found to be the same for both chloride-fluoride and chloride melts. However, in the case of chloride-fluoride melt, the content of magnesium, aluminium and silicon in the electrolyte is higher than pure chloride melt. Probably this is associated with the increase in the partial dissolution currents of electronegative elements in passing from chloride to chloride-fluoride melt or higher solubility of oxofluoride compounds. While the higher content of magnesium in the electrolyte does not lead to its higher concentration in the metal, the situation is worse for aluminium and silicon for which their concentrations rise by an order of magnitude. After electrorefining, the oxygen concentration remains rather high 0.01-0.03 wt%. A major contribution to the total oxygen concentration comes from the oxide film formed during treatment of the cathode deposit. Analysis for oxygen content after removal of the oxide film (treatment depth 5  $\mu\text{m}$ ) by spark mass spectrometer gives values in the range  $1 \cdot 10^{-3}$ - $4 \cdot 10^{-3}$  wt%.

A simple criterion for prediction of the distribution coefficients of chromium and impurities for electrorefining process has been suggested.

## CONTRIBUTION OF THE SPECTROPHOTOMETRY TO THE HIGH TEMPERATURE MOLTEN SALT CHEMISTRY

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The interest of CEA (French Atomic Energy Commission) in pyrochemistry is renewed for the development of future fuel cycle. We then undergo studies on actinides in molten halides. For the moment, samples are taken off from molten solutions, solubilized in aqueous media and then studied by classical methods (ICP-AES, alpha and/or gamma spectroscopy...). This procedure produces harmful radioactive liquid waste with halides, hard to treat in our nuclear facility. Spectrophotometry could be an attractive method to perform in situ analyses without producing such liquid waste. In molten salts, the absorption bands are due to electronic transitions between f-energy levels and are described in literature. Nevertheless, there are very few results on spectrophotometry in chloride or fluoride molten salts, mainly qualitative. Therefore, in order to use the spectrophotometry on a quantitative point of view, it is necessary first to acquire the values of molar extinction coefficients as a function of the temperature for the most representative absorption bands of the species of interest. Information on repeatability and reproducibility are also necessary.

A vertical furnace with a 25 mm well, fitted with an horizontal optical axis and high temperature optodes were specially developed. Directly introduced in the optical axis of the furnace, they are connected to the spectrophotometer by optical fibers. A quartz reactor was used to maintain samples under inert atmosphere. In chloride media, commercial optical quartz cells were used, but in fluoride media, very corrosive, windowless cells in nickel or graphite were selected. These cells were developed in Oak Ridge in the 60's to study corrosive melts by mean of spectrophotometry or Raman spectroscopy.

A demonstrative study was carried on neodymium in LiCl/KCl between 350 and 550°C and in LiF/AlF<sub>3</sub> between 750 and 850°C.

In chloride media, with quartz cells, it is possible to determine the behavior of five characteristic bands. These results were applied to the determination of the solubility of NdCl<sub>3</sub> in LiCl/KCl as a function of the temperature and the kinetic of dissolution of NdCl<sub>3</sub> in the same salt, at a given temperature.

In fluoride media at 800°C, with windowless cells, it is more difficult to record spectra which are noisy particularly under 450nm and over 750nm. Nevertheless, it is possible to determine the behavior of two bands. These cells were used to study a reductive extraction of neodymium from the salt to molten aluminum. The distribution coefficient of the neodymium between the two phases, already measured by classical analysis, has been confirmed by this way.

The experimental apparatus was easy to use, especially in chloride media with quartz cells. In fluoride media, the windowless cells were quite difficult to manipulate and the results were not very precise. An evolution of the cell is necessary either to obtain more quantitative results or to obtain data on the kinetic of transfer.

This apparatus will be used soon to study the behavior of actinides in molten salts.



## **SOME PRELIMINARY RESULTS ON MODIFIED TITANIUM DIBORIDE COATINGS PRODUCED BY ELECTROCHEMICAL SYNTHESIS FROM MOLTEN SALTS**

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### **ABSTRACT**

Titanium diboride coatings modified with co-deposited iron have been obtained on steel substrates by electrochemical synthesis from NaCl-KCl-NaF-K<sub>2</sub>TiF<sub>6</sub>-KBF<sub>4</sub>-FeCl<sub>2</sub> electrolyte at 700 °C with titanium used as anode. It was found that the non-modified titanium diboride coating is approximately 3 times thicker than the modified coating obtained on the same substrate under the same experimental conditions (note: the thickness of the non-modified coating is 47.4% of the theoretical value, whereas that of the modified coating is only 14.3%). It has been shown that the dissolution of steel (that is, substrate material) in the electrolyte is the main reason for such low current efficiency of the synthesis. However, further investigation is needed to understand the reason(s) why the thicknesses of the two coatings (modified and non-modified) differ so much from each other. Adhesion to the substrate surface of the modified and non-modified coatings has been compared. It has been shown that such a modification significantly improves the adhesion.

### **ACKNOWLEDGEMENTS**

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## NMR STUDY OF MOLTEN FLUORIDE IN PRESENCE OF GRAPHITE

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We present preliminary results on the interactions between the molten fluoride salts with graphite as seen by NMR spectroscopy.

The graphite electrodes are grinded and mixed with fluoride salt. The mixed powders are put in boron nitride crucibles, that are hermetically closed. The whole operation is done in gloves box filled with dry Argon in order to prevent the formation of oxide complex upon melting. The crucible is heated by a laser CO<sub>2</sub> in the cryomagnet and is protected by a flux of Argon. The NMR spectra are recorded a few degrees above the melting temperature. In order to study the effect of temperature and heating duration in melt, the samples are first heated for different times in a furnace under Argon and then cooled at room temperature, before NMR experiments.

The studied salts are LiF pure or mixed LnF<sub>3</sub> with Ln=La, Nd, Y, with various compositions (95%-5%, 90%-10%, 80%-20%).

For short times, only one peak is observed around 200ppm. As the time is increased a second peak appears at lower chemical shift. In the same time, the relaxation time T<sub>1</sub> is strongly decreasing.

# CLUSTER MODEL STRUCTURE OF ALKALI METAL CHLORIDE MELTS

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As it was earlier<sup>1</sup> reported, we started examining cluster model structures of alkali metal chloride melts. The structures consist of  $C3^-$  or  $C3^+$  clusters (including three coordination spheres of  $M^+$  or  $Cl^-$  ions, respectively) and outersphere (OS) ions  $M_2Cl^+$  or  $MCl_2^-$ . The principal geometric parameters of these structures are the distances  $d(M-Cl)$ : in the cluster –  $d(cl)$ , between the cluster and OS ion within the layer –  $d(os)$ , between clusters located in adjacent layers –  $d(l)$ . For the calculation of potential energies (PE) of element interaction within the structure and the  $d(M-Cl)$  values the Pauling's potential was used because its precision is sufficient for a quality analysis ( $\sim 0.001$  nm for geometric parameters).

This work presents the results of calculation of energies and geometric parameters for structures ( $C3^- \cdot M_2Cl^+$ ). The parameters of these structures are closer to experimental than those of structures ( $C3^+ \cdot MCl_2^-$ ). The only exclusion is CsCl for which the above structures have close parameters. The calculations were carried out for two cluster types, i.e. for "perfect" clusters with all ions occupying normal lattice positions, and for "equilibrium" clusters whose parameters were determined by minimizing the cluster PE. It appeared that equilibrium clusters have great excess energy as compared with perfect clusters. It is assumed that this energy is consumed on rotation of OS ions and on appropriate increasing of the  $d(os)$  geometric parameter (in comparison with its equilibrium value). Two variants have been considered: 1) rotation of initial OS ions  $M_2Cl^+$  and 2) rotation of  $MCl$  ions which are formed due to OS ions dissociation. It is found that only the second variant ensures the molar volume values of melts close to experimental values.

So, the structure of alkali metal chloride melts, both within this model and accuracy of the calculations, is described by a combination of interacting clusters  $C3^-$ , molecules  $MCl$  and ions  $M^+$ .

## Acknowledgement

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## Reference

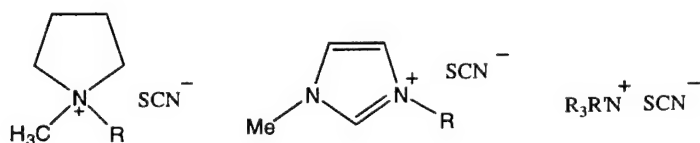
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## ORGANIC SALTS OF THE THIOCYANATE ANION.

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Research into the design and development of more environmentally benign, cleaner chemical processes with reduced pollution potential is a primary driving force within the field of green chemistry. The potential utilization of room temperature ionic liquids as replacements for conventional organic solvents is of considerable interest and as part of the ongoing research into these materials a new series of ionic liquids is reported based on the thiocyanate anion. Incorporation of this anion with an imidazolium, tetraalkyl ammonium or pyrrolidinium cation produces ionic liquids with advantageously low melting points and good thermal stability.



In common with many other pyrrolidinium salts the thiocyanates have rich thermal behavior in the solid state, with several phases being displayed, and these have been analyzed using Differential Scanning Calorimetry (DSC). Cyclic voltammograms of representative pyrrolidinium and imidazolium species are reported as an initial indication of their potential in electrochemical applications. In addition the solid state structure of *N,N*-dimethyl pyrrolidinium thiocyanate has been analyzed using x-ray crystallography. This is the first reported structure of a quaternary ammonium thiocyanate species.

## GALVANOSTATIC PHASE FORMATION AT THE ELECTRODE -MOLTEN SALT INTERFACE

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Under galvanostatic conditions of nucleation and growth of new phase the supersaturation varies substantially during electrodeposition. An important feature of this process is the interdependence between the nucleation kinetics and the nucleus growth one. In this case the transfer of the substance to the electrode takes place under non-stationary conditions. The appearance of nuclei leads to a redistribution of the current at the electrode.

For the description of this process the computer simulation method was used [1]. With the help of this method the nuclei parameters are introduced into memory of the computer and their evolution is monitored.

For the calculations the experimental values of the parameters of electrodeposition of silver on platinum in nitrate melts were used [2]. The analysis of calculated data makes possible to reveal the main regularities of galvanostatic formation and growth of new phase.

Following the current switching on the double layer is charged up, the adatom concentration grows and the overpotential increases. After a certain interval of time the first nucleus appears and beginning from this moment a part of the current is used up for the growth of this nucleus. The adatom concentration at which the first nucleus evolves is several percents (1-5) of the concentration of fully filled silver monolayer. If the nucleus growth current does not exceed the external current the overpotential continues to grow and the next nuclei are formed.

At low current densities ( $10^{-3}$ - $10^{-4}$  A·cm<sup>-2</sup>) only one nucleus is formed on the electrode. According to calculations the exchange current density at the molten salt - nuclei interface is ( $10^2$ - $10^3$ ) A·cm<sup>-2</sup>.

The exchange current density at the molten salt - new phase interface can be determined also with the help of the potentiostatic current transients in the process of three-dimensional phase formation [3].

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## MOLTEN SALT THERMAL STORAGE FOR GAS TURBINES

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The production of coal in Australia produces close to 7% of Australia's greenhouse gas emissions, mostly through fugitive emissions of methane. Unfortunately, although methane is a valuable fuel as natural gas, 2/3rds of the methane from coal mines is diluted to a low concentration (< 1.25 %). In addition this concentration is highly variable with fluctuations of up to 400% in a single day. Not only is this gas difficult to burn but the large fluctuations in concentration make the heat generated by combustion difficult to utilise.

A gas turbine system is currently being developed which uses molten salt thermal storage to even out these fluctuations. The ventilation and drainage gas from the mine is introduced directly into the gas turbine compressor with a concentration range of approximately 0.8 to 1.2%. The compressed gas is then heated to approximately 530°C via recuperation with the turbine expander's exhaust gases and is then passed into a catalytic combustor where it combusts. The combustion products, now with a range of temperatures between 650 and 950°C, passes through a heat exchanger imbedded in molten salt. The latent heat of the change of phase in the molten salt is used to buffer out the fluctuations in temperature caused by the fluctuations in methane concentration. This system stores the chemical energy of the methane gas as heat as an alternative to trying to physically store the low concentration gas. Physically storing the gas is not practical because of the gas's low concentration which results in a very high volume. The use of storage means that a turbine system can be designed to use the average concentration of gas from the mine rather than the minimum flow. This can result in a far greater mitigation of greenhouse gases.

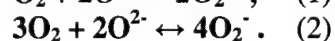
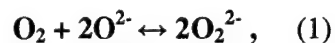
Two molten salt thermal storage containers with different air to salt heat exchange mechanisms have been constructed and tested. The first experiment uses a single heat exchanger tube surrounded by molten salt in a cylindrical vessel. The salt under test is an equimolar eutectic of Lithium Carbonate and Potassium Carbonate and has a melting point of 505°C. An electrically heated heat exchanger was used to heat the air before it was fed to the storage vessel. A range of temperatures both above and below the melting point of the salt were tested to determine the temperature rise along the heat exchanger. Air pressures from 1 to 6 atmospheres were tested with the salt remaining at 1 atmosphere. The rate of heat transfer to and from the salt along was compared to a theoretical axisymmetric finite volume model. A second experiment was also conducted which bubbled the air through a molten salt to measure the direct contact heat transfer. The direct contact technique offers the promise of far greater heat transfer than the indirect contact heat exchanger and the possibility of molten salt oxidation of the low concentration methane. This paper describes the results from these preliminary experiments together with an overview of future research.

## THE ELECTROCHEMICAL REDUCTION OF OXYGEN IN MOLTEN ALKALI CHLORIDES: THEORETICAL CONSIDERATION

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The dissolved oxygen reduction in molten alkali chlorides often is an interfering process during electrochemical production of different metals and alloys. The experimental data [1] on the oxygen interaction with the molten NaCl, KCl and CsCl indicated the existence of higher oxides with concentrations comparable with those of the dissolved oxygen molecules estimated basing the ionic melt hard sphere model. These species, namely peroxide ( $O_2^{2-}$ ) and superoxide ( $O_2^-$ ) as well as the oxygen molecules ( $O_2$ ) might be involved into the electrode reactions. In this case the oxygen reduction could be considered as a complicate totally thermodynamically reversible electrochemical process including the following chemical reactions between diffusing particles:



The process of oxygen reduction in the melts over the partial oxygen pressure and total oxide concentration ranges from  $10^4$  to  $10^5$  Pa and from  $10^{-2}$  to 1 mole/m<sup>3</sup> correspondingly was considered. The balances of mass and charge as well as the mass action law equations for equilibrium (1) and (2) were taken into account. The variations of concentrations of all electroactive particles ( $O_2$ ;  $O_2^-$ ;  $O_2^{2-}$ ;  $O^{2-}$ ) over diffusion layer were calculated under different cathodic current densities. It allowed finding the particle mass flows (expressed in electrical units) and estimating the value of the potential of the indifferent electrode under specified experimental conditions. The oxide ion ( $O^{2-}$ ) was shown to be the basic product of oxygen reduction independently of a current density value. At the same time oxygen transport to the electrode surface complicates with increasing current density starting from  $O_2$  molecules only under low current densities and becoming  $O_2$  plus  $O_2^-$  and  $O_2$  plus  $O_2^-$  plus  $O_2^{2-}$  under intermediate and limiting ones respectively. At the limiting current densities the values of mass flow of  $O_2$  molecules and superoxide  $O_2^-$  ions are almost equal each other. Therefore the polarization curve of oxygen reduction in molten alkali chlorides can be described by the following equation:



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# IONIC CONDUCTIVITY OF MOLTEN $\text{PCl}_5 - \text{MCl}_n$ (M – POLYVALENT METAL) MIXTURES

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The electrical conductivity of molten mixtures of phosphorus pentachloride with s-, p- and d-polyvalent metal chlorides is measured in temperature range from 300 to 750 K under raised vapour pressures. It is found that the mixing melts of low-conducting salts such as  $\text{PCl}_5$ ,  $\text{ZrCl}_4$ ,  $\text{TaCl}_5$ ,  $\text{MoCl}_5$ ,  $\text{ZnCl}_2$ ,  $\text{BeCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{AlCl}_3$ , and  $\text{FeCl}_3$  results in the elevating electrical conductivity, which achieves that of typical ionic salts (see Fig.).

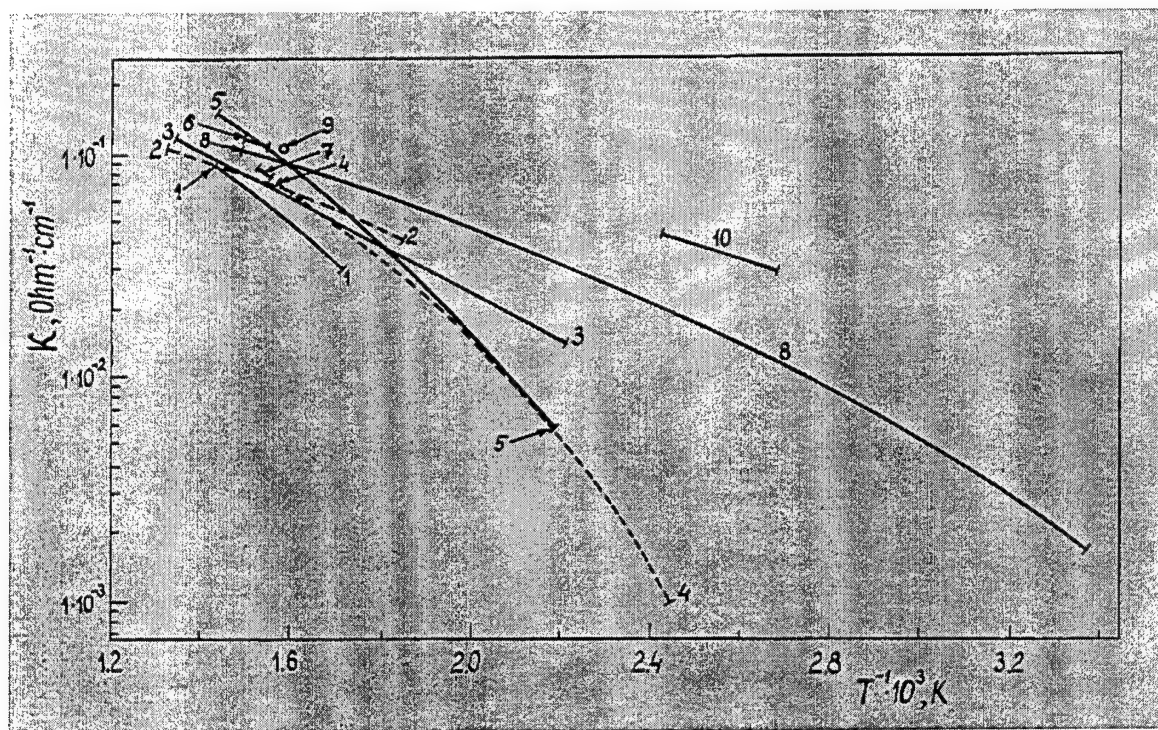


Fig. Temperature dependence of the specific conductivity of molten  $\text{PCl}_5 - \text{MCl}_n$  mixtures containing 30-50 mole %  $\text{PCl}_5$ :  $\text{ZrCl}_4$  (1),  $\text{TaCl}_5$  (2),  $\text{MoCl}_5$  (3),  $\text{ZnCl}_2$  (4),  $\text{BeCl}_2$  (5),  $\text{SnCl}_4$  (6),  $\text{TiCl}_4$  (7),  $\text{AlCl}_3$  (8),  $\text{FeCl}_3$  (9),  $\text{ICl}$  (10)

It is of interest that the specific conductivity of all studied molten mixtures containing 30-50 mole %  $\text{PCl}_5$  is practically constant within a limit of experimental error. The regularities revealed for the most of molten salt compositions including phosphorus pentachloride are due to the formation of complex anions and cations making possible the charge transfer.



**Structure of lead silicate glasses in the system  $\text{Na}_2\text{O-PbO-SiO}_2$  :  
 $^{29}\text{Si}$ ,  $^{23}\text{Na}$  and  $^{207}\text{Pb}$  solid state NMR study**

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The incineration of industrial wastes leads to the formation of amorphous solids containing variable amounts of toxic elements. In Romania, large amounts of residues issue from car batteries incineration containing corrosive materials and heavy metals are usually dumped without any treatment in landfills. Immobilization in silicate glasses is known to improve the leaching behaviour of wastes, and then to limit ground waters pollution.

Compositions of these glasses are complex, and a first structural approach can be performed on simplified matrixes. In this study, we have investigated by multinuclear ( $^{29}\text{Si}$ ,  $^{23}\text{Na}$ ,  $^{207}\text{Pb}$ ) solid state NMR a series of lead silicates glasses in the ternary  $\text{Na}_2\text{O-PbO-SiO}_2$  system with a PbO content varying from 11 to 26 mol.%. This allows to describe the local structure around each cation in the glass network.

The  $^{29}\text{Si}$  MAS NMR spectra evidence several distinct resonances that can be assigned to  $\text{Q}_2$ ,  $\text{Q}_1$  and  $\text{Q}_3$  units with relative intensities that reflect the polymerisation degree of the silicate network. Broadband  $^{207}\text{Pb}$  VOCS NMR spectra indicate that the major part of lead atoms are likely to occur as  $\text{PbO}_3$  or  $\text{PbO}_4$  pyramids (Pb at the apex) with the existence of Pb-O-Si bonds.  $^{23}\text{Na}$  MAS and triple-quantum MAS spectra were recorded to give a description of the glass network from the modifier point of view and  $^{29}\text{Si}/^{23}\text{Na}$  TRAPDOR (**TR**Ansfer-of-**P**olarisation-in-**D**ouble-**R**esonance) experiments were used to characterize the spatial proximities between the  $\text{Na}^+$  modifier cations and the different  $\text{SiO}_4$  tetrahedra ( $\text{Q}_n$ ).

## NMR signature of Al dissolution in NaF-AlF<sub>3</sub> melts

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Cryolite-based melts used in the Hall-Heroult electrolytic process for the production of Aluminium have been studied by NMR at high temperature. In situ NMR experiments have been performed in the ternary NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> system up to 1030°C with the observation of the different nuclei present in the system, <sup>27</sup>Al, <sup>23</sup>Na, <sup>19</sup>F and <sup>17</sup>O. We can propose now a structural description of these liquids in terms of different aluminium bearing species that coincides rather well with the Raman data given by B.Gilbert et al. supporting the existence of AlF<sub>5</sub><sup>-</sup> species. Moreover, the <sup>17</sup>O NMR spectra give a selective and quantitative description of alumina dissolution in molten Cryolite. From the evolution of <sup>17</sup>O and <sup>27</sup>Al chemical shifts with Al<sub>2</sub>O<sub>3</sub> additions in the melt, we can confirm the existence of different Al-O-F species in the melt by mean of their direct experimental evidence.

This study have been extended to the characterisation of metallic aluminium dissolution in the cryolitic melts. In the industrial cells, the metal produced is heavier than the bath and falls down on the bottom of the cell. The metal is then in contact with the electrolyte and the graphite container and can induce secondary reactions that will influence strongly the electrical rate of the process. The aluminium solubility in molten cryolite is always a subject of discussion. Compared to the other metals-molten salts systems, the system Al-NaF-AlF<sub>3</sub> is considerably more complex. In addition of the Al dissolution in the salt, one must take into account the exchange reactions as  $\text{Al} + 3\text{NaF} \rightleftharpoons \text{AlF}_3 + 3\text{Na}$ , and the appearance of new species. This is expressed through the NMR spectra, and their complex evolution with metal contents and temperature.

# A NEW FAMILY OF ROOM TEMPERATURE MOLTEN SALTS BASED ON THE 1-ALKYL-2-METHYL PYRROLINIUM CATION

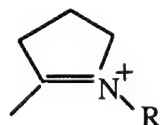
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<sup>a</sup>School of Physics and Materials Engineering, <sup>b</sup>School of Chemistry

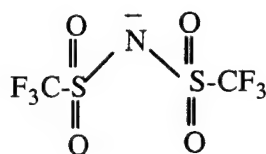
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Room temperature molten salts (also known as ionic liquids) have long been known and investigated for a number of applications in electrochemistry and electrochemical devices. However, interest has expanded recently<sup>1,2</sup> because of the unique properties that room temperature molten salts offer as benign solvents for "green" synthesis of important chemical products. In previous reports<sup>3,4</sup> we have described the synthesis and properties of ionic liquids in the quaternary ammonium and N-alkyl-N-methyl pyrrolidinium cation families.



**Pyrrolinium Cation**



**TFSA**

A number of new organic salts of the 1-alkyl-2-methyl pyrrolinium cation (where alkyl = Et, Pr, Bu and anion = iodide or bis[trifluoromethane sulfonyl] amide, TFSA) were synthesized and characterized in this work. The characterization results of this new family of salts, including thermal properties, density, viscosity, conductivity and electrochemical stability, will be presented. Of these salts, the iodide salts have melting points around 100 °C while the amide salts have melting points around room temperature. Two of the amide salts can be easily quenched into the glassy state and exhibit glass transition temperatures around -70 °C. The two liquid salts at room temperature exhibit ionic conductivity in the range of 10<sup>-3</sup> S.cm<sup>-1</sup>. The electrochemical window of stability for these molten salts was found to be about 4V and one of these salts presents good thermal stability up to 400 °C. The 2-methyl pyrrolinium cation bears structural similarities to the aromatic imidazolium cations on one hand and the cyclic ammonium cation family based on the pyrrolidinium cation on the other. The properties of the salts reported here will be compared within these two related families of salts.

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## ELECTROCHEMICAL BEHAVIOUR OF RARE EARTHS IN MOLTEN CHLORIDES. APPLICATION OF ELECTROCHEMICAL TECHNIQUES IN PYROCHEMICAL PROCESSES

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This work takes part of a research line between the Department of Analytical Chemistry (UVA) and CIEMAT, concerning the study of the feasibility of pyrometallurgical processes in order to separate actinides and lanthanides. The determination of thermodynamic data of solutions as well as the electrochemical behaviour of the elements are of crucial importance for the understanding of the process and the design of the separation cell.

The electrochemical behaviour of some REs such as Ce, La, Pr, Y and Nd ions after chlorination of the samples with gaseous HCl, was investigated in two molten chlorides with different oxoacidity properties (LiCl-KCl and CaCl<sub>2</sub>-NaCl) using i) solid and ii) liquid Cd electrodes.

### i.- Metal electrodeposition studies onto solid cathodes.

Electrochemical techniques provide an efficient tool for investigating the reaction mechanisms. Preliminary experiments showed that refractory metals such as tungsten and molybdenum are convenient electrode materials in both melts, it is not possible to use glassy carbon due to formation of Na-C or Li-C compounds.

The kinetic parameters of the reaction steps are calculated from transient techniques taking into account the diffusion's contribution of electroactive species, electron transfer, kinetics and additionally adsorption or crystallisation, the last one generally is controlled by the rate of nucleus formation and the diffusion of active species.

Activation energies for diffusion and diffusion coefficients of REs have been obtained, and the validity of the Arrhenius law was verified.

### ii.- Metal electrodeposition studies onto liquid cathodes.

The electrode reactions of the RE(III)/RE couples at the surface of a liquid Cd electrode were investigated by cyclic voltammetry at 673, 723, 773 and 823 K in LiCl-KCl eutectic melt. The redox potentials of the RE(III)/RE couple at the liquid Cd electrode were observed at more positive potentials than those at the solid electrodes. These potentials shifts were thermodynamically analyzed by a lowering of activity of REs in the Cd phase due to the formation of the alloys LnCd<sub>11</sub> and YCd<sub>6</sub> at the interphase.

As well as the Gibbs energy of formation of LnCd<sub>11</sub> and YCd<sub>6</sub> the Gibbs energy of formation of other intermetallic compounds could also be estimated by the analysis of the peaks in cyclic voltammograms of the Re(III)/RE redox systems at a Cadmium thin film planar electrode.

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## SOLUBILIZATION OF RARE EARTH OXIDES PRESENT IN A SIMULATED NUCLEAR FUEL IN MOLTEN CHLORIDES.

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The present work is a part of a research project that studies the feasibility of several pyrometallurgical processes in order to separate actinides (U) from the fission products contained in a simulated nuclear fuel. One of these processes consists of the chlorination of the oxides and the subsequent metal electrodeposition. The achievement of this goal requires a good knowledge of both the chemistry of these elements in molten chlorides and their electrochemical behaviour. Therefore elementary data of these elements in molten halogenides is a major concern.

Solubilization studies of rare earth oxides and oxohalides contained in a SIMFUEL have been carried out in the eutectic LiCl-KCl melt at 450°C and the equimolar CaCl<sub>2</sub>-NaCl mixture at 550°C. First, chlorinating conditions were predicted by comparing the E-pO<sup>2-</sup> diagram of the different rare earth-O compounds to that of several chlorinating gaseous mixtures. In order to build up the potential-acidity diagrams, the stability of the oxidation states of rare earth (RE = La, Ce, Nd, Pr and Y), the standard potential of the different red-ox couples and the solubility product of oxides and oxychlorides were determined in both molten chlorides at the temperatures studied.

Oxidation states (III) and (0) were found to be stable in both molten chlorides for all RE. For neodymium, Nd(II) was also found to exist. The standard potential values of the different red-ox couples were also determined by combining both potentiometry and cyclic voltammetry and allowed to obtain the activity coefficient of RECl<sub>3</sub> compounds in the molten media. It was found that RE(III) cations were less solvated by the chloride ions in the calcium melt, which was explained by formation of CaCl<sub>4</sub><sup>2-</sup> ions. Moreover it was demonstrated that, at a given working temperature, the rare earth cations with higher polarizability (higher charge to ionic radius values) are also more solvated by the melt.

Solubilization tests of RE-O samples showed that in the case of using gaseous Cl<sub>2</sub> as chlorinating agent, the kinetics of the chlorinating reaction was much slower than that of gaseous HCl, even when using the mixture Cl<sub>2</sub>(g)+C(s).

**Acknowledgements.-** Authors thank to ENRESA (Spain) for the financial support (CIEMAT-ENRESA and CIEMAT-UNIVERSIDAD DE VALLADOLID agreements).

Some aspects of the work has been performed under the 5<sup>th</sup> Framework Programme of EC within the project Pyrometallurgical processing research programme "PYROREP" (FIKW-CT-2000-00049)

## ELECTRODEPOSITION STUDIES OF MAGNESIUM IN THE EUTECTIC LiCl-KCl MIXTURE

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The necessity for optimisation of the electrodeposition process of Mg in molten chlorides has led to many investigations concerned with it. For this reason, research studies of the effect of some of the main causes for losses in current efficiency, have been carried out. The work presented here is a continuation of a series of studies initiated at the Department of Materials Technology and Electrochemistry, in Trondheim, Norway, in order to elucidate the different and complicated phenomena that take place during magnesium electrodeposition. The understanding of these processes may facilitate proper choice of the electrode material and melt compositions and could help in the optimisation of the industrial process of magnesium production.

The current efficiency of the electrolytic process depends critically on the purity of the feed material, in this case the quality of the anhydrous magnesium chloride feed, and it is typically in the range 85-90%.

The work is focussed on one of the causes for losses in current and energy efficiency during the process: i.e. interactions between the deposit and the substrate (nucleation and growth phenomena of the magnesium phase). Results obtained in the eutectic LiCl-KCl mixture containing different MgCl<sub>2</sub> concentrations will be discussed. The working temperature was varied in order to run experiments above and below the melting point of magnesium. Tungsten was used as cathode material. Electrochemical techniques such as cyclic voltammetry, chronopotentiometry and chronoamperometry were employed in order to characterise the system and study nucleation and growth phenomena of the magnesium phase.

One of the most remarkable features was the significant UPD of lithium, which makes the effect of macroscopic growth of the deposit more pronounced. This phenomena was observed by voltammetry, chronopotentiometry and chronoamperometry. The growth of the magnesium deposit was easier noticed when magnesium was formed in the solid state than as a liquid.

**Acknowledgements.-** The Research Council of Norway and Norsk Hydro ASA are acknowledged for financial support. A.M.Martínez wishes also to thank the "Secretaría de Estado de Educación y Universidades" (Spain) for a post-doctoral grant.

## ADVANCED IONIC LIQUIDS: ZWITTERIONIC LIQUIDS

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Although ionic liquids show quite high ionic conductivity,<sup>1</sup> it is impossible to realize the target ion conduction in the ionic liquids. To overcome this drawback, new ionic liquids have been designed.<sup>2</sup> One is the zwitterionic liquid in which both cation and anion were tethered as shown in Figure 1.<sup>3</sup> Although these zwitterionic liquids contain no carrier ions, they showed relatively high ionic conductivity of about  $10^{-5} \text{ S cm}^{-1}$  at ambient temperature when LiTFSI was added to them. The lithium transference number ( $t_{\text{Li}^+}$ ) of zwitterionic liquid containing equimolar amount of LiTFSI is 0.56. Generally,  $t_{\text{Li}^+}$  in typical organic solvents is below 0.4. In addition, zwitterionic liquids are non-volatile. Therefore, these zwitterionic liquids are regarded as new non-volatile solvents for ionic materials.

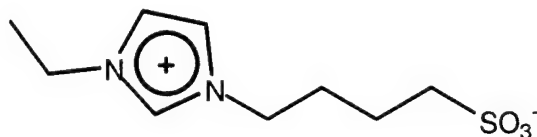


Figure 1 A structure of zwitterionic liquids.

On the other hand, zwitterionic liquids were recently used as dual solvent-catalysts for organic reactions.<sup>4</sup> As new functions can be added to zwitterionic liquids by the addition of acids, bases, salts, and so on, these zwitterionic liquids will be used in various areas. They are expected as the next-generation ionic liquids.

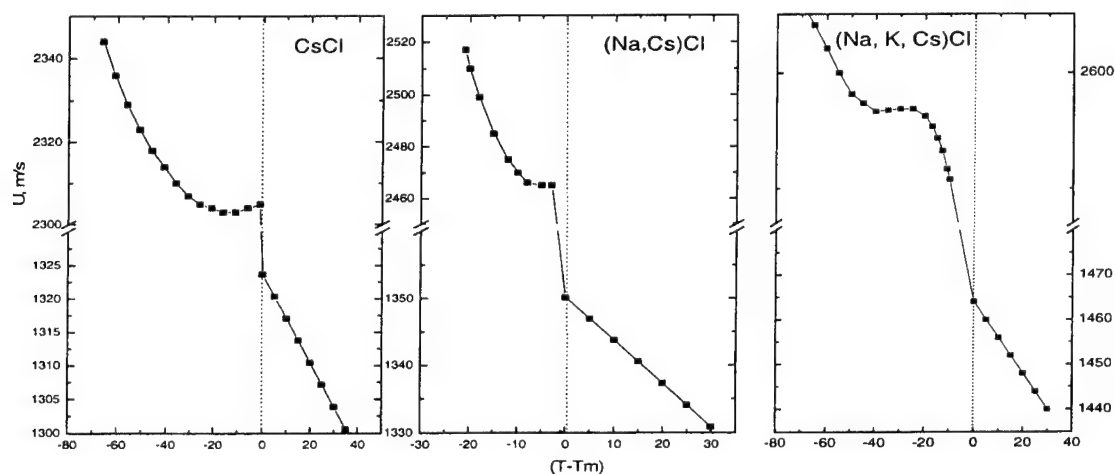
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## New Data on the Ultrasonic Velocity in Crystalline Alkali Chloride Eutectics Close to the Melting Point

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The ultrasonic velocity ( $u$ ) in crystalline and molten caesium chloride as well as NaCl-CsCl and NaCl-KCl-CsCl eutectic mixtures near the melting point is measured by the propagation of sound wave method. It is found that the ultrasonic velocity decreases linearly in dependence on temperature in melts while change of this parameter in solid is extraordinary. Contrary to the usual linear temperature dependence of sound velocity in ionic crystals observed in wide temperature range that in solid caesium chloride and above eutectic compositions distorts close to the melting point, as indicated in Figure presented below.



**Fig.** Velocity of ultrasound propagation in crystalline and molten CsCl and NaCl-CsCl and NaCl-KCl-CsCl eutectic mixtures near the melting point

Three peculiarities can be noted. The first is deviation of the  $u$  as the function of temperature from linearity. The second is a drastic decrease of the ultrasonic velocity in several degrees  $\Delta T = T_{am} - T_m$  prior to the melting point  $T_m$  up to its value for corresponding molten compound. The third is clear dependence of  $\Delta T$  on chemical composition of the salt sample being tested. Indeed, as the CsCl concentration decreases the  $\Delta T$  rises and the slope of the  $u/\Delta T$  curve diminishes progressively once the  $T_{am}$  is achieved.

Like distortions at the same temperature range were observed by us earlier for temperature dependences of the lattice parameter, thermal conductivity and thermal diffusivity of individual alkali halides and their eutectic mixtures. They have been ascribed to formation of cooperated defects in ionic crystal lattice.

Radically new phenomenon first detected only in ultrasonic investigation is the apparent fall in the melting point of both pure salt and eutectic salt mixtures. It is probably caused by the action of ultrasonic wave (mechanical vibrations) on the unstable imperfect crystal lattice close to the phase transition temperature.



## Prediction of Physicochemical Properties of the Selected Fuel Salt Compositions

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In this paper the predicting ways of the physicochemical properties such as the density ( $\rho$ ), the dynamic viscosity ( $\eta$ ), the isobaric heat capacity ( $c_p$ ), and the thermal conductivity ( $\lambda$ ) are proposed for two types of FLIBE based ternary fuel salt mixtures in the Na,Li,Be /F and Li,Be,Th/F systems for the MSR.

The calculation algorithm was based on the addition principle for the properties ( $P_x$ ) of multi-component salt mixtures, which can be found from the relationship  $P_x = \sum N_i \cdot P_i$ . Here  $N_i$  and  $P_i$  denote mole fraction and corresponding property of individual molten salts or their binary mixtures as constituents of the more complex systems. The closer the composition of initial and selected melts, the more reliable is the prediction, which usually is connected with an interpolation of the input data. Unknown properties of Na,Li,Be /F and Li,Be,Th/F melts may be estimated by using the available experimental data on the molten LiF-NaF, LiF-BeF<sub>2</sub>, NaF-BeF<sub>2</sub>, LiF-ThF<sub>4</sub>, and NaF-ThF<sub>4</sub> mixtures. The properties of ternary salt mixtures are predicted within the limits of experimental error of measuring the density, the dynamic viscosity, the isobaric heat capacity, and the thermal conductivity of molten alkali fluorides and binary melts above mentioned. It is significant that the calculation technique used is based on very limited volume of the experimental data.

The estimated values of the several fuel compounds (solvents) are presented below in Table.

### The predicted values of the density, viscosity, heat capacity and thermal conductivity of the selected fluoride melts

Property	Molten salt composition		
	0.07 LiF – 0.642 NaF – 0.288 BeF <sub>2</sub>	0.143 LiF – 0.59 NaF – 0.267 BeF <sub>2</sub>	0.22 LiF – 0.567 NaF – 0.213 BeF <sub>2</sub>
$\rho$ (g·cm <sup>-3</sup> )			
800 K	2.1592	2.1514	2.1473
1000 K	2.0560	2.0456	2.0397
$d\rho/dT$ (g·cm <sup>-3</sup> ·K <sup>-1</sup> )	$5.16 \cdot 10^{-4}$	$5.29 \cdot 10^{-4}$	$5.38 \cdot 10^{-4}$
$\eta$ (centipoises)			
800 K	11.28	10.48	8.92
1000 K	4.33	4.13	3.72
$c_p$ (cal·g <sup>-1</sup> ·K <sup>-1</sup> )			
800÷1000 K	0.515	0.529	0.540
$\lambda$ (W·m <sup>-1</sup> ·K <sup>-1</sup> )			
800 K	0.82	0.84	0.87
1000 K	0.92	0.94	0.97

# STUDY OF THE ANODIC GASES COMPOSITION DURING Nd<sub>2</sub>O<sub>3</sub> – MgO ELECTROLYSIS IN FLUORIDES MEDIA

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Mg – Nd alloy has been obtained by the electrochemical co-deposition of Nd and Mg on a metallic Mo cathode. The electrolyte was a ternary system NdF<sub>3</sub> – LiF – MgF<sub>2</sub> and the raw materials for the electrolysis process were Nd<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and MgCO<sub>3</sub>.

There were determined the chemical compositions of the anodic gases during the electrolysis at different current densities and distances between electrodes.

A special electrolysis installation has been used for experiments, having the anode made from super dense graphite and the cathode made from metallic Mo (fig.no.1).

The special shape of the anode is made so as to improve the evolution and the collection of the anodic gases.

A chromatograph CARLO ELBA 4200 was used for gases analyses, with silicagel for the adsorption columns and He as carrier gas.

The experimental results (fig.no 2, 3) indicate that the content of CF<sub>2</sub> + C<sub>2</sub>F<sub>6</sub> is less than 2% vol, only at anodic effect the content increases at 18 – 20 % vol.

The anodic critical current density is greater than 0.45 A/cm<sup>2</sup>, fact which allows favourable conditions for an efficient electrolysis process.

The total content of the carbofluorides in the anodic gases increases very slow with the increase of the MgO (MgCO<sub>3</sub>) content in molten electrolyte.

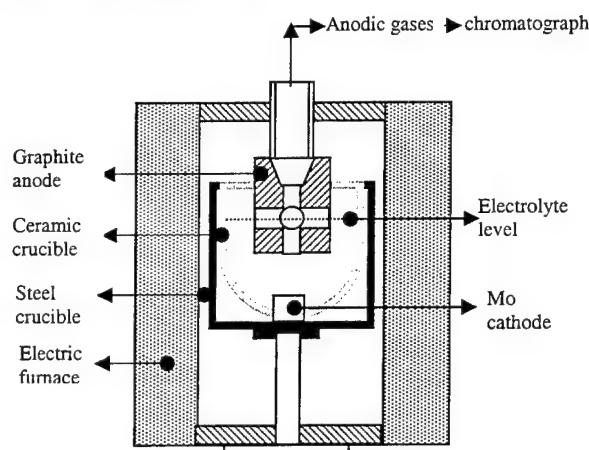


Fig. no. 1. Cross section of the experimental installation

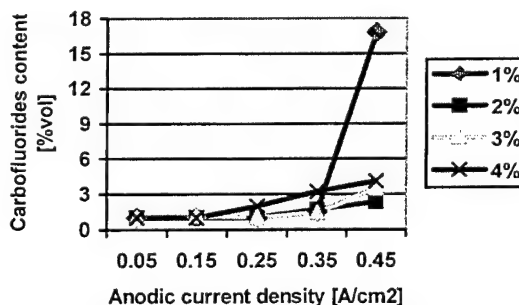


Fig. no. 2 Carbofluorides content versus  $D_A$  for (1 – 4% wt) MgO

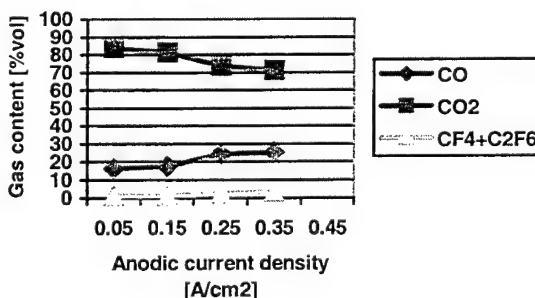


Fig.no.3. Gases contents versus  $D_A$  for 8.36% MgCO<sub>3</sub> in the molten electrolyte

Acknowledgement: This research is sponsored by NATO's Scientific Affairs Division in the framework of the Science for Peace Programme.

# SOLUBILITY AND DISSOLUTION KINETIC OF THE $\text{Nd}_2(\text{CO}_3)_3$ IN MOLTEN FLUORIDES

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$\text{Nd}_2(\text{CO}_3)_3$  can be used instead of  $\text{Nd}_2\text{O}_3$  as raw material for the metallic Nd obtaining by electrolysis in molten fluorides.

This fact is due to the very small dissolution rate of the  $\text{Nd}_2\text{O}_3$  in the electrolyte.

There were studied the solubility and dissolution kinetics of the  $\text{Nd}_2(\text{CO}_3)_3$  in ternary system  $\text{LiF} - \text{NdF}_3 - \text{MgF}_2$  at different temperatures

The analyze method was the determination of the total oxygen content in the oxyfluorides melts using an EXHALOGRAPH BALZERS EOA 220 apparatus.

The  $\text{O}_2$  content analyze consists in the carbothermal reduction of the sample with the forming of CO, which is detected by infrared spectroscopy.

The working temperature during the analyze by EXHALOGRAPH was over  $2400^\circ\text{C}$ ; at this temperature the carbothermal reaction is total.

The solubility of the neodymium carbonate is comparable to the neodymium oxide solubility; for example at  $850^\circ\text{C}$ , the oxygen content is 0.1966 wt% for carbonate and 0.192 wt% for oxide.

The solubility increases with the temperature increase having the maximum value 0.3388  $\text{O}_2$  wt% at  $1000^\circ\text{C}$ . (Table 1.)

The dissolution rate for the neodymium carbonate is greater than the oxide, the necessary time to reach the equilibrium being 3 hours in comparison with the oxide where the equilibrium time is 8 hours. (Figures 1 and 2).

Table 1.  $\text{Nd}_2(\text{CO}_3)_3$  solubility in the 62.82  $\text{NdF}_3 - 27.18 \text{LiF} - 10 \text{MgF}_2$  (wt%) system:

Solubility at equilibrium			
Temperature [ $^\circ\text{C}$ ]	Time [h]	Concentration [wt%]	
		$\text{O}_2$	$\text{Nd}_2\text{O}_3$
800	4	0.1617	1.133
850	3	0.1960	1.373
900	3	0.2200	1.542
1000	2	0.3388	2.374

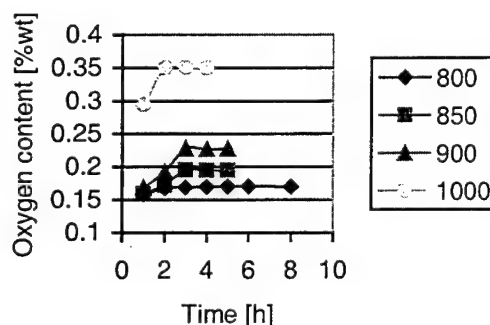


Fig.1 Kinetic study of the  $\text{Nd}_2(\text{CO}_3)_3$  dissolution. Oxygen content versus time at different temperatures

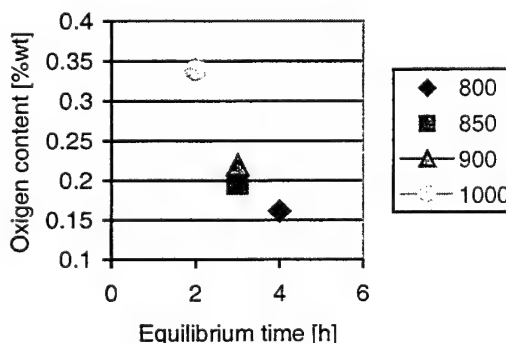


Fig.2. Kinetic study of the  $\text{Nd}_2(\text{CO}_3)_3$  dissolution. Oxygen content at equilibrium time.

## SPECTROSCOPIC INVESTIGATION OF COBALT(II) CHLORIDE COMPLEXES IN ACETAMIDE – AMMONIUM NITRATE MELT

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Formation of cobalt(II) complexes with halide ions in various aqueous or non-aqueous solvents has long been known. The co-ordination number of cobalt(II), geometry and colour of its complexes often depends on the ligand used. A change from octahedral pale red  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complex to intense blue tetrahedral  $[\text{CoCl}_4]^{2-}$  upon addition of hydrochloric acid in aqueous solutions is well known [1]. Similar change in co-ordination occurs when chloride is added to cobalt(II) solutions in nitrate melts.

In the present study absorption spectra of cobalt(II) chloride in acetamide – ammonium nitrate mixture have been investigated. The mole fractions of the acetamide and ammonium nitrate were 0.723 and 0.277 respectively. Melting point of this mixture is nearly 40 °C and absorption spectra have been studied and recorded at two different temperatures (45 and 60 °C). In the absence of chloride ions, the absorption spectra of cobalt(II) show absorption maximum at 538 nm, typical for octahedral co-ordination of cobalt. Addition of  $\text{NH}_4\text{Cl}$  caused a shift of the absorption maximum toward lower energies and increase of the molar absorption coefficient. The chloride containing melts show three distinct absorption maxima at 610, 628 and 650 nm, typical for tetrahedrally coordinated cobalt complexes. However, the molar absorbance in the chloride containing melts increases with temperature, in contrast to the normally expected behaviour of tetrahedral complexes. Such a behaviour of cobalt chloride complexes in the acetamide – ammonium nitrate solvent mixture may be the result of mixed complex formation with solvent molecules (or ions) and chloride ions, the structure of these mixed complexes being very much dependent on temperature [2].

The stability constants, the number of absorbing species and the species spectra have been calculated using the non-linear regression program STAR [3]. From a large number of trials to obtain the most relevant complexation model, it was concluded that the following species are formed:  $[\text{Co}(\text{NO}_3)_4]^{2-}$ ,  $[\text{Co}(\text{NO}_3)_2\text{Cl}_2]^{2-}$ ,  $[\text{CoCl}_4]^{2-}$ . The overall stability constants of these complexes were calculated at 45 and 60 °C.

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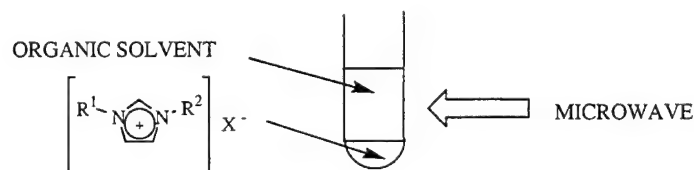
## New Approaches to Synthesis: Microwave-Mediated Chemistry Using Ionic Liquids

Nicholas E. Leadbeater and Hanna M. Torenus\*

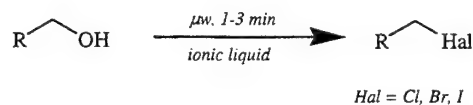
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Synthetic chemists are looking for new ways to prepare target molecules selectively, rapidly and in high yields. Microwave-mediated synthesis is an area of increasing interest due to the fact that it is often possible to greatly accelerate the rates of reactions and on many occasions new chemistry can be developed. In addition, the selectivity of reactions is often very high. One of the drawbacks of microwave-mediated chemistry is that a highly polar solvent such as DMSO, DMF or 1-methyl-2-pyrrolidone (NMP) is often required. We present here the results from our investigations into the development methodologies for facilitating the microwave heating of non polar solvents such as hexane.<sup>1</sup> Building on an idea first presented by Ley and co-workers,<sup>2</sup> we have achieved this by using small quantities of ionic liquids as additives as illustrated below.



Ren and Wu has shown that ionic liquids can be used as reagents for synthesis. They have used them for the room temperature conversion of alcohols to alkyl halides in the presence of either an organic or inorganic acid but reaction times are very long (generally 24 to 48 h).<sup>3</sup> We have shown that it is possible to greatly accelerate this reaction by using microwave irradiation. Starting from primary alcohols, we can form the desired halides in good yields in between 1 and 3 min.



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## Electrochemical study of rare earths in molten (Li, K)Cl eutectic for dry reprocessing of hydrogen absorbing alloys

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Hydrogen absorbing alloys have been utilized as anode activating material in secondary batteries not only for portable electronic devices but also for electric vehicles. Currently, most of the hydrogen absorbing alloys in commercial base are categorized as AB<sub>5</sub> (A: rare earths, B: Ni, Fe, etc) type due to their lower production costs and better charge-discharge characteristics for repeated use. Rare earths are not "rare" elements, however, 70% of these are produced at localized area, e.g. China, North America and Russia. If the demands for rare earths increase rapidly even in developing countries, one should make an effort to recycle the metals from the batteries currently in use.

Thus, we suggest one of the optional techniques of rare earths separation from hydrogen absorbing alloys by using molten salt media. The procedure constitutes of the following 3 electrochemical techniques.

- 1) Rare earths are anodically electro-dissolved into ionic melt bath from spent hydrogen absorbing alloys.
- 2) Rare earth cations are then concentrated near the anode area in the column by using the countercurrent electromigration method.
- 3) Rare earths are finally cathodically electro-deposited in metallic form. Depending on the concentration and current density, separation of each rare earth would be feasible.

The advantages of the suggested procedure are the compact system, simplicity of the process, and the additional possibility of reducing secondary wastes.

As a first step, several electrochemical measurements under different operating conditions have so far been performed to check the feasibility of processes 1) and 3). Differential pulsed voltammograms show clearly the difference of electro-deposition and electro-dissolution potentials between molten (Li, K) eutectic mixture systems containing different rare earths, i.e. La, Ce and Nd as previously shown in [1]. Especially, in the system containing Nd, the disproportionation reaction is confirmed. We have also performed practical tests of electro-deposition in some cases, and these results will be shown at the poster presentation.

<sup>†</sup>This study is supported by Industrial Technology Research Grant Program in '02 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan

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## DIRECT ELECTROLYTIC PREPARATION OF CHROMIUM POWDER

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Powder metallurgy is preferred to traditional melting and casting technologies for producing and processing metal alloys, particularly those containing metals of very different reactivities, densities and melting points. Chromium is an important constituent of not only various stainless steels but also many specialty alloys, for example, the special high-duty nickel or cobalt based super alloys. In the latter cases, chromium powder is needed for production. Chromium powder also finds uses in composite materials such as cermets (ceramic-metal) that have special properties required in various commercial applications, for example, electrodes, cutting tools and aerospace components.

Commercial chromium powder is currently produced by grinding and milling lump forms of chromium that are mainly produced by two methods: aluminothermic reduction of chromium oxide, and electrolytic deposition from aqueous solutions of chromium compounds, e.g. the so called *chrome alum*,  $\text{CrNH}_4(\text{SO}_4)_2$ . Typical challenges associated with the grinding/milling process include high energy consumption, variation in particle sizes and contamination by mill materials.

This presentation reports a novel electrolytic process for producing chromium powder directly from chromium oxide powder in molten  $\text{CaCl}_2$  and its eutectic mixture with  $\text{NaCl}$ . In the process,  $\text{Cr}_2\text{O}_3$  powder is made the cathode on which the main reaction is  $\text{Cr}_2\text{O}_3 + 6e = 2\text{Cr} + 3\text{O}^{2-}$ . The  $\text{O}^{2-}$  anion (or  $\text{CaO}$ ) then diffuses to and discharges at the anode. [GZ Chen, DJ Fray, and TW Farthing, *Nature*, 407 (2000) 361. GZ Chen and DJ Fray, *Progress in Molten Salt Chem.*, vol. 1, eds. Berg, R.W. and Hjuler, H.A., Elsevier, Paris, (2000)157.] Electrolysis voltage and temperature were in the ranges of 2.5~3.1 V and 700~950°C, respectively. Current efficiency of 70~80 % was attained with the product containing oxygen at commercially satisfactory levels (1000~3000 ppm). The product, in the form of small pellets when removed from the molten salt, could be manually crushed into a powder, allowing the solidified electrolyte to be easily removed by dissolution in water. Electron microscopy revealed that, see Fig.1, the powder was composed of unique cubic chromium particles of uniform sizes (5~20 micrometers). A 3-phase interline propagation mechanism is proposed to account for the electro-reduction of the solid metal oxide to the metal in molten salts. Calcium intercalation into the chromium oxide cathode is suggested for low voltage electrolysis.

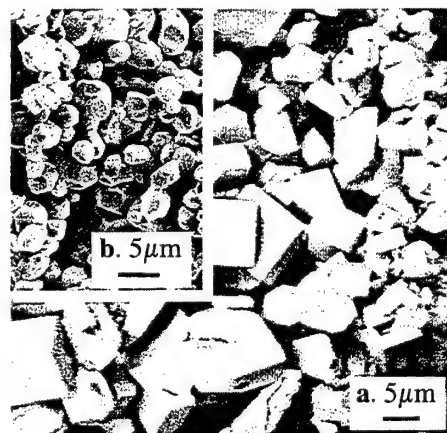


Fig. 1. SEM images of chromium powder (a, main frame) prepared by electrolysis of solid  $\text{Cr}_2\text{O}_3$  (b, insert) in molten  $\text{CaCl}_2$ .

<sup>†</sup> Academic visitor (July~Sept. 2000), Dept of Mater. Sci. and Metall. Eng., Universidad Carlos III de Madrid, Avda. de la Universidad, 30, 28911 LEGANÉS (MADRID), SPAIN



## Electrolytic Reduction of Solid Titanium Dioxide to Titanium Metal in Molten Calcium Chloride<sup>‡</sup>

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Although titanium is the fourth most common structural metal in the earth's crust, its use, compared to other common metals, is restricted due entirely to the complicated and expensive method of extraction. Titanium metal has a very high affinity to oxygen and in order to avoid oxygen contamination of the final product; the oxygen is removed by the carbo-chlorination of the oxide to produce titanium tetrachloride vapour which is then reduced by magnesium to titanium and magnesium chloride with the latter being removed by distillation. This process was discovered in 1940 and the inventor, William Kroll, predicted in early 1950's that his process would be replaced by an electrochemical one within fifteen years. This prediction has not been fulfilled although there have been many attempts, all unsuccessful on a large scale for a variety of reasons, e.g. failure to reach desired purity levels or difficulties with the reactivity of the product. Recently, Okabe *et al* [*Metall. Trans. B* 24 (1993) 449-455.] reported the electrochemical removal of oxygen from solid titanium, by making titanium pieces (wire and foil) the cathode in a molten salt such as calcium chloride. The proposed mechanism is that on the application of a cathodic current, calcium is deposited on the titanium, either reacts directly with the oxygen to form calcium oxide which dissolves in the melt or dissolves in the melt and then reacts with the dissolved oxygen. Calcium oxide is more stable than titanium oxide and, as it dissolves in the electrolyte, the activity of the calcium oxide is reduced which makes the reaction for the removal of oxygen even more favourable. It should be noted that calcium and other Group II chlorides have a large solubility for their oxides.

An alternative explanation is that, if one examines the possible cathodic reactions, it can be seen that the ionisation of oxygen or the reduction of oxides to metal and oxygen ions takes place at a less cathodic potential than the cathodic reaction for the deposition of calcium. This opens up the prospect of being able to directly reduce the oxide to metal purely electrochemically without the deposition of calcium. In order to test the feasibility of this concept, small pellets of pressed and sintered titanium dioxide powder were placed in a crucible of either graphite or titanium, the crucible filled with molten calcium chloride and a voltage well beneath the decomposition voltage of calcium chloride applied between a carbon anode and the wall of the crucible. On removing the pellets after electrolysis and washing, it was noticed that it had turned a metallic grey colour and examination under the scanning electron microscope showed that the 0.25  $\mu\text{m}$  oxide powder had been transformed into 12  $\mu\text{m}$  titanium metal particles. The anode gases consisted mainly of oxygen with a small amount of carbon dioxide and monoxide, in accordance with other studies of carbon with oxygen at moderate temperatures.

This technique, now called the FFC Cambridge Process by the industry, can be applied to many other metal oxides (e.g. oxides of zirconium, niobium, rare earths, uranium and plutonium whose physicochemical properties resemble  $\text{TiO}_2$ ) and becomes a generic technology.

<sup>‡</sup> This poster was prepared for the previous EUCHEM 2000 Conference on Molten Salts ( 20-25 Aug. 2000, Karrebaeksmide, Denmark) but was not submitted for financial reasons. Its re-submission to this conference aims at complementing other presentations from the Cambridge Materials Chemistry Group.



## MICROSTRUCTURE DESIGN IN THE SYSTEMS Na//F, Cl, CO<sub>3</sub>, R (R=MoO<sub>4</sub>, WO<sub>3</sub>)

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Four-component Na//F, Cl, CO<sub>3</sub>, R (R=MoO<sub>4</sub>, WO<sub>3</sub>) systems and bordering them ternary ones had been investigated experimentally (for instance, [1,2]). Two compounds: congruent NaCl.NaR and incongruent NaF.NaR were founded. Quasi-ternary section NaF-Na<sub>2</sub>CO<sub>3</sub>-NaCl.NaR divides the system to eutectic and eutectic-peritectic sub-systems. Literature data are confined to only co-ordinates of nonvariant equilibrium points and to not very accurate drawings (rather to a scheme of the phase diagram concentration projections). However even so poor information makes possible to construct the model of the phase diagram (PD) as nine liquidus equations. Described by them hypersurfaces are satisfactory nearly experimental determined eutectic and peritectic points. Equations will be corrected if any additional information will be known.

The phase diagram of the system Na//F, Cl, CO<sub>3</sub>, R consists of 75 hypersurfaces. Among them 63 hypersurfaces are ruled ones including 30 with generating lines and 33 with generating planes. Projections of not all upper borders but also of all preceding phase reactions regions borders to every three- and four-phase region concentration space divide the region to fragments. These fragments are distinguished by conditions of the phase reaction fulfillment in the presence of moved there from another regions crystals. And the conditions materials formation with the unique set of micro- and nano-structure elements within every of these four-dimensional fragments and on their boundaries are differed. As a result among 35 phase regions of the given PD 26 are divided into fragments. In total it is 129. Projections of 75 hypersurfaces of the PD to the concentration tetrahedron break it into 90 three-dimension fields. It is the result, taking into account two-, one- and zero-dimension fields, 299 variants of microstructure.

Both geometrical and then computer models of the PD make possible to solve various tasks of heterogeneous design such as: the investigation of the PD by any sections; the calculating experiment for the definition of the PD parameters at the preliminary stage before further experimental investigation; the testing of the experimental data correspondence to geometrical thermodynamics regularities; the mass quota calculation of coexisting phases and different origin crystals; the prediction of possible compounds and the determination of

concentration and temperature conditions of the materials construction according to given microstructures and properties.

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## SYNTHESIS OF COMPLEX TITANIUM AND ZIRCONIUM OXIDE NANO-POWDERS IN MOLTEN NITRATES.

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Increased interest in obtaining powders of complex oxides in the medium of ionic melts arose from possibility to decrease temperature of synthesis and, consequently, to obtain highly active powders consisting of structured nano-particles [1-3].

Alkali metal nitrates and nitrites hold much promise for the synthesis of complex oxides. They are melted at low temperature and complex oxides are slightly soluble in their melted medium.

We studied these nitrate and nitrite melts as the reaction medium for obtaining complex oxides. The composition of complex oxides is varying about zirconium or titanium dioxides. In order to ground synthesis in melts theoretically, thermodynamic calculations were carried out, a kinetic model and a model of formation of nano-powders were developed. It was determined experimentally that acid-base properties of the melts have an influence on the rate and selectivity of reaction. The content of cation impurities of potassium metals in final products is subjected this influence as well.

The synthesized oxide powders were identified by means of X-ray phase analysis (diffractometer "Dron 3M", Cu-K $\alpha$ ), chemical analysis and electronic microscopy. The reaction kinetics was studied by methods of TG, DTG, DTA and chemically analyzing the medium after termination of interaction.

The powders of doped zirconium dioxides and zirconates were obtained and separated from the melts as nano-particles (5-15 nm) with narrow distribution of sizes. Sizes of titanate powders are 60-150 nm. Formation of particles with such big sizes is explained by utilization of insoluble titanium dioxide as a precursor material.

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## IONIC INTERACTIONS OF ACTINIDE HALIDES

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We follow our earlier studies of actinide tetrahalides [1] and rare-earth halides [2] and construct a microscopic model for the ionic interactions in actinide trihalides. We determine the overall trends of the model parameters for the trivalent actinide metals in their trihalides. We present a brief comparative study of lathanide and actinide halides.

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## STRUCTURE OF RARE-EARTH/ ALUMINIUM HALIDE COMPLEXES

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We evaluate the structure and binding of various complexes that are formed in binary systems of rare-earth halides with aluminium halides. Our calculations are based on an ionic model that was originally developed for Al chloride molecules and molecular ions entering Al chloroaluminates [1]. For the interactions between rare-earth ions and chlorine and fluorine ions, we have made use of our earlier results on rare-earth chloride [2] and fluoride [3]. The model thus includes an account of the electronic polarizability of the rare-earth ion, in addition to the electronic and short-range overlap polarizabilities of the halogen. We carry out calculations of the structure for a number of these molecules, selected in such a way as to allow us to expose the structural trends holding across the whole series of compounds.

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## APPLICATION OF OXIDIMETRY FOR DETERMINING SPECIATION OF VB-GROUP METALS IN MOLTEN CHLORIDES

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When investigating the physico-chemical behaviour of VB-group metals in chloride melts it is important to know and control their speciation. For this purpose we propose using oxidimetric method. The general idea of this technique lies in red-ox titration of melt samples, quenched in an inert atmosphere. Ammonium vanadate is suggested as a suitable titrating agent, which does not oxidise chloride-ions. Upon addition of an excess of the oxidant, vanadium is converted into tetravalent state and niobium and tantalum into pentavalent Nb(V) and Ta(V), respectively. Unreacted ammonium vanadate is then back-titrated using a suitable reducing agent, *e.g.*, iron(II). Knowing the total concentration of the studied metal in quenched electrolyte and determining the amount of the oxidant used in the oxidation reaction the integral oxidation state of the metal can be determined.

This method can only be employed when the red-ox potential of the species of interest is sufficiently separated from the deposition potential of the alkali metal. Electrochemical properties of vanadium, niobium and tantalum in chloride melts allow using this technique in order to follow the red-ox reactions in which these metals take place.

The oxidimetric method is particularly effective when used in conjunction with other techniques, both electrochemical and spectroscopic.

We have applied this method when investigated the chlorination reactions of VB-metals in a wide temperature range using chlorine and hydrogen chloride and established the regimes of the processes. The conditions necessary for the formation in the melt vanadium, niobium and tantalum compounds in various oxidation states have also been determined. The effects of temperature and flow rate of the chlorinating agent on the speed of the process were also investigated.

Use of the oxidimetry method for studying the process of interaction of metals with the melts containing their ions was also quite effective. The influence of various factors on the course of the reactions was established. Using the obtained data, together with the information from the oxidimetric, coulombometric and potentiometric studies of the anodic dissolution of vanadium, niobium and tantalum, it was found that mainly vanadium(II), niobium(III) and tantalum(IV) ions are present in the equilibrium with the respective pure metals. When interpreting the result it was necessary to take into account the influence of certain external factors, for example, the reactions of VB-metal species in the lower oxidation states with quartz often used as a material for constructing high-temperature experimental cells.

## Joint electrodeposition of molybdenum and tungsten and products molybdenum-tungsten alloys, double carbides from oxihalide melts

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From literature data it is known that sodium oxifluoromolibdate is not stable in halide melts. We tried to determine the range of concentrations of an oxihalide melt in which the oxifluoride complex  $\text{MoO}_2\text{F}_4^{2-}$  is stable. Also the processes of joint electroreduction of tungsten and molybdenum oxifluoride complexes in chloride-fluoride melts have been investigated.

The electrochemical behaviour of the  $\text{KCl-NaCl-NaF}(2.5-7.5 \text{ wt. } \%)$ - $\text{Na}_3\text{MoO}_3\text{F}_3$ - $\text{Na}_3\text{WO}_3\text{F}_3$  system has been studied at  $750^\circ\text{C}$  by methods of linear and cyclic voltammetry.

We suppose that two kinds of electrochemically active species -  $\text{MoOF}_6^{2-}$  and  $\text{MoO}_2\text{F}_4^{2-}$  are formed in the  $\text{KCl-NaCl-NaF-Na}_3\text{MoO}_3\text{F}_3$  melt when the ratio  $[\text{F}^-]/[\text{MoO}_3]$  is higher than 25. Two waves at potentials  $-0.6-0.75 \text{ V}$  and  $-1.0-1.1 \text{ V}$  versus quasi-reversible platinum/oxygen reference electrode corresponding to the reduction processes of  $\text{MoOF}_6^{2-}$  and  $\text{MoO}_2\text{F}_4^{2-}$ -ions are observed in the voltammograms. When the ratio  $[\text{F}^-]/[\text{MoO}_3]$  is lower than 25, the reduction of a more stable complex  $\text{MoO}_2\text{F}_4^{2-}$  at potentials  $-0.9-1.0 \text{ V}$  takes place.

The reduction process of the complex  $\text{WO}_2\text{F}_4^{2-}$  in the  $\text{KCl-NaCl-NaF-Na}_3\text{WO}_3\text{F}_3$  melt proceeds in a similar way at potentials  $-1.0-1.1 \text{ V}$ . Small additions of  $\text{Na}_3\text{MoO}_3\text{F}_3$  to the melt do not lead to the appearing of new waves in the voltammogram, neither cathodic nor anodic. These additions only make the reduction wave shift to the area of more positive potentials by  $0.1-0.15 \text{ V}$ , and decrease its slope.

Similar processes happen when  $\text{Na}_3\text{WO}_3\text{F}_3$  is added to the melt containing  $\text{Na}_3\text{MoO}_3\text{F}_3$ . Sodium tungstenate additions to the melt allow to prevent the formation of intermediate  $\text{MoOF}_6^{2-}$  complex, which is unstable, and the process becomes more stable.

Therefore, controlling fluoride- and oxide-ions' activities, it is possible to realise the processes of joint electroreduction of  $\text{WO}_2\text{F}_4^{2-}$  и  $\text{MoO}_2\text{F}_4^{2-}$  complexes and obtain tungsten-molybdenum alloys.

The joint reduction  $\text{WO}_2\text{F}_4^{2-}$ ,  $\text{MoO}_2\text{F}_4^{2-}$  and  $\text{CO}_2$  in chloride-fluoride melts containing oxide-fluoride complexes of tungsten and molybdenum  $\text{WO}_2\text{F}_4^{2-}$ ,  $\text{MoO}_2\text{F}_4^{2-}$  under excessive pressure of carbon dioxide is realized too. In voltammetric curves, one wave elongated along the potential axis corresponds to the process of joint electroreduction of these species. However, the strict quantitative dependence of the current on the carbon dioxide pressure was not received. Apparently, this is caused by the instability of chloride-fluoride system containing tungsten and molybdenum oxide-fluoride complexes.

Potentiostatic electrolysis of the chloride-fluoride melts containing  $\text{WO}_2\text{F}_4^{2-}$  and  $\text{MoO}_2\text{F}_4^{2-}$ -ions and  $\text{CO}_2$  yields double carbides of tungsten and molybdenum, and also solid solutions of tungsten and molybdenum carbides.

**DETERMINATION OF THE LIQUIDUS IN A COMPUTER SIMULATION OF THE  
Li/KCl MIXTURE, AND A STUDY OF THE IONIC STRUCTURE AT THE  
SOLID/LIQUID INTERFACE**

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By employing a large simulation cell containing a crystalline and liquid region, we are able to directly determine the equilibrium conditions (i.e. P and T) for the co-existence of a pure solid (either KCl or LiCl) with an Li/KCl liquid of varying composition. The liquidus may then be extracted (i.e. the melting temperature at one atmosphere as a function of the composition). The results are in excellent agreement with experiment, especially when polarization effects are included in the interaction potential.

We have also studied the ionic structure across the interface between the solid and liquid phases at various liquid compositions. The results show appreciable penetration of the Li ions into interstitial positions in the KCl crystal which is in equilibrium with the K-rich liquid.

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## CHEMLA EFFECT IN Li/KCl: A COMPUTER SIMULATION STUDY

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Using molecular dynamics, we calculated the internal mobilities for the two cations with respect to Cl) in the Li/KCl mixture at different compositions. The mobilities show evidence of a Chemla crossing point on the Li rich side of the composition diagram at sufficiently low temperatures, in agreement with the experimental data. It was shown that the composition-dependence of the mobilities is not simply related to that of the diffusivities. However, it does parallel the behaviour of the decay rates of the "cage-correlation functions", which give the timescales on which the contents of the coordination shell of anions about the two types of cations change. This well-defined property seems to be a quantitative measure of Okada's self-exchange velocity, and the results support the dynamicdissociation model.

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## RAMAN SPECTRA OF IONIC LIQUIDS: INTERPRETATION VIA COMPUTER SIMULATION

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Raman spectra of the complex-forming ionic liquids  $\text{LaCl}_3$  and  $\text{ScCl}_3$ , derived from molecular dynamics computer simulations, are presented. These simulations, which use polarizable ion interaction models, have previously been shown to predict structural properties in excellent agreement with diffraction experiments. The dependence of the polarizability of the melt on the ionic positions, which determines the Raman spectrum through the time-dependence of the polarizability correlation function, is modelled on the basis of *ab initio* electronic structure calculations carried out on alkali chlorides. New simulation techniques are introduced in order to allow the spectrum to be calculated with acceptable statistics. The calculated spectra are in semi-quantitative agreement with experimental data. The distinctive bands which appear in the spectra of such complex melts are linked to the vibrations of the transient coordination complexes which form in these melts and new interpretations for the origin of several well-known features are proposed. The simulations thus enable a link between the structure of a melt as perceived through Raman spectroscopy and through diffraction experiments to be made.

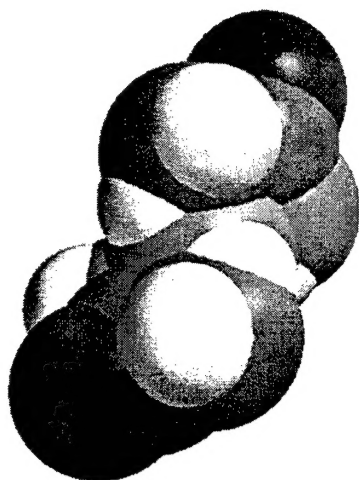
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## New Solvent Systems Based on Eutectic Mixtures of Quaternary Ammonium Salts and Hydrogen Bond Donors

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This work describes the properties and applications of novel ionic liquids based on choline-like ammonium salts with hydrogen bond donor molecules. We have developed a large number of easily prepared, air and moisture stable liquids to study the differing chemical nature of each mixture.<sup>1</sup> These liquids exhibit unusual solvent properties that are strongly influenced by hydrogen bonding. In general, compounds capable of donating or accepting hydrogen bonds show high solubilities. For example, in a 1 choline chloride: 2 urea mixture high solubilities are observed for inorganic salts (*e.g.*  $\text{LiCl} > 2.5 \text{ mol dm}^{-3}$ ), salts that are sparingly soluble in water (*e.g.*  $\text{AgCl}$  solubility  $> 0.66 \text{ mol dm}^{-3}$ ), aromatic acids (*e.g.* benzoic acid solubility  $> 0.82 \text{ mol dm}^{-3}$ ) and amino acids (*e.g.* D-alanine solubility  $> 0.38 \text{ mol dm}^{-3}$ ). Also, because these liquids have strong ligating effects they are capable of dissolving several metal oxides *e.g.* solubility of  $\text{CuO} > 0.12 \text{ mol dm}^{-3}$  typically only soluble in harsh acidic media. The conductivity and viscosity of these media are also discussed and applications of these liquids are demonstrated with novel chemical synthesis and metal deposition.



Packing Model for Chloride-Urea Interaction

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## PHOSPHORUS SPECIES IN CRYOLITE-BASED MELTS

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Aluminium is produced industrially by electrolytic reduction of aluminium oxide dissolved in a NaF-AlF<sub>3</sub> based melt at ~950°C. Impurities entering the electrolyte from the raw materials influence process parameters like current efficiency and metal quality. Phosphorus is an increasingly important impurity element in the Hall-Heroult process due to more recycling of impurities with secondary alumina and limits on the phosphorus content in aluminium.

Previously we have investigated the behaviour of phosphorus by adding AlPO<sub>4</sub> to an alumina-saturated cryolite melt at 1000 °C [1]. It has been found by Tkatcheva et al. [2] that when not conducting electrolysis the phosphate anion is a stable species in cryolite-based melts. So far our voltammetric studies showed that the 5-valent phosphorus is reduced to P(III). The diffusion coefficient was determined to be  $1.5 \cdot 10^{-5}$  cm<sup>2</sup>/s at 1000 °C. Currently we are investigating by means of different electrochemical methods how phosphorus ions can be reduced further in these melts. Additions of different phosphorus-containing salts to cryolite based melts will show if the reduction mechanism is influenced by the type of phosphorous compound added. The effect of changes in bath composition and temperature will be presented as well.

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# **Cation Composition of a Solvent as a Highly Effective Tool for Control over the Chemical and Phase Composition of the Products of Electrochemical Synthesis of Refractory Metals Compounds in Molten Salts**

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Oxygen-containing refractory metal species draws attention of many researches in recent years. Such interest stems from the need to obtain reliable information on the electrochemical behaviour of this harmful impurity in niobium, tantalum, tungsten or zirconium. In addition, the problem of oxygen in electrolysis of refractory metal compounds has taken on a new significance over the last decade. This is associated with the possibility of synthesizing electrochemically novel compounds, specifically in the systems Nb-O, Nb-O-F, Nb-F-Me, Nb-O-F-Me, and Ta-O-Me, Ta-O-Me-F (Me is an alkali metal) and also tantalum with tetragonal lattice which is unusual for this metal.

Alkali metal chlorides and fluorides are used as solvents for basic constituents of molten electrolytes ( $K_2NbF_7$ ,  $K_2NbOF_5$ ,  $K_3NbO_2F_4$  etc.). It is well known that the nature of the anion in a solvent has a profound effect on the electrochemical behaviour of refractory metal and oxygen in melts. At the same time, the role of the cation composition of a solvent in the electrochemical process has remained out of the focus. This is reflected in a limited and nonfunctional choice of solvents employed in practice. The equimolar mixture NaCl-KCl and ternary LiF-NaF-KF eutectic (FLINAK) are the most frequently used. However, such an approach of a solvent is often too simplified and restricts the amount of information that can be obtained in electrochemical studies. Indeed, we may assume *a priori* that the outer-sphere surroundings of niobium or tantalum complex anions, composed of solvent cations, should influence the structure and stability of these complexes and hence their electrochemical behaviour.

In this work we pioneered in examination of the character of influence of individual alkali-metal cations ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$  and  $Cs^+$ ) in fluoride and chloride solvents on the electrochemical reduction of niobium and tantalum complexes in melts with different O/Nb or O/Ta ratios, more specifically, on the chemical and phase composition of the cathodic products of electrolysis. Our findings show that this influence may be determining factor in the cathode phase formation at electrodeposition. Varying the cation composition of solvent from Li to Cs allows one to obtain cathodic products over wide limits of compositions in the electrochemical synthesis of new compounds:

Nb, Nb(O), NbO', Nb<sub>4</sub>O<sub>5</sub>, tetragonal suboxide Nb<sub>6</sub>O, rhombohedral suboxide Nb<sub>x</sub>O ( $x < 6$ ), composite (laminated) compounds "NbO"•  $n$ "MeF" (Me = K, Rb;  $n = 1, 2$ ) for niobium-containing melts and Ta of tetragonal crystal form and novel tantalum bronzes of three crystal structure types: tetragonal, hexagonal and cubic one with potassium or sodium as alkali metal constituents for tantalum-containing melts.

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## INDEX OF MAIN AUTHOR/PRESENTER

(Key: **PL** Plenary; **K** Keynote; **C** Contributed Oral; **P** Poster)

Aguado, A	K5
Akdeniz, Z	P55, P56
Angell, C A	PL5
Babushkina, O	P11
Bermejo, R	P41
Bessada, C	K4, P38
Bhatt, A	C20
Billard, I	P19
Boiko, O	C24
Bourg, S	P28
Branco, L C	P9
Brennecke, J F	K9
Bukatova, G	P25
Capper, G	P62
Castrillejo, Y	P40
Chen, G Z	P51, P52
Chrissanthopoulos, A	P20, P23
De Long, H C	K2
Elizarova, I	P24
Endres, F	K1
Esina, N O	P14
Fray, D J	PL1
Freyland, W	PL4, P7
Gadzuric, S B	P48
Gontcharenko, E A	P10
Graetzel, M	PL6
Grinevitch, V V	P64
Hamel, C	P17
Hardacre, C	K13
Holbrey, J D	K7
Isaev, V A	P33
Iwadate, Y	P18
Kazmierczak, J	P8
Khokhlov, V	C15, P35, P36, P44, P45
Kisza, A	C10, P8
Kremenetsky, V	P31
Kushhov, H B	C5, P6, P58
Kuznetsov, S A	C15, P26, P27
Lanning, O	P59
Lans, S C	C3
Lynden-Bell, R M	K12
Madden, P A	P61
Markus, T	C1
Martinez, A M	P42
Massot, L	C16, P16
Matsuura, H	C8, P50
May, I	P12
Mendoza, L	K11
Mirnaya, T A	C18, P13
Morgan, B	P60

Nuta, I	P3, P37
Ohno, H	C19
Ohtori, N	C7, P21, P22
Okabe, T	PL2
Okada, I	C9
Okoturo, O O	C25
Olsen, E	C4
Papatheodorou, G N	PL3
Price, D L	K3
Pringle, J	P32
Ribeiro, M C C	C6
Ritchie, A	C22
Rogers, R D	K15
Rollet, A-L	P30
Soare, V	P46, P47
Soucek, P	P15
Stefanidaki, E	P4
Sudovtsova, L	P1
Sun, J	P39
Sytchev, J	P29
Thisted, E W	P63
Thonstad, J	C12
Titov, A A	P5
Torenius, H M	P49
Trulove, P	K10
Volkov, S V	P54
Volkovich, V A	C13, P57
Vorob'eva, V	C21, P53
Welton, T	K14
Welz-Biermann, U	C23
Wendt, M	P34
Woodcock, L V	C17
Yan, X Y	C16
Yolshina, L A	C2, P2
Yoshizawa, M	P43
Zell, C	K6